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ON CERTAIN SULPHAMIDO DERIVATIVES OF FURFURANE.[1]

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The object of this research was to determine whether sulphinides could be formed in the furfurane series. Of the two methods for preparing these bodies in the aromatic series, that[2] by oxidation of orthomethylsulphamides was inadmissible here, because of the instability of the furfurane ring toward oxidizing agents. Accordingly, all the work was done by the second method,[3] consisting in treating with ammonia the chloride of an ortho-β-sulphocarboxyl acid. We have studied in this way three different pyromucic acids, β-sulpho-δ-methylpyromucic acid,[4] β-sulpho-δ-chlorpyromucic acid,[5] and β-sulpho-δ-brompyromucic acid.[1] Each of the first two of these acids was treated with phosphoric pentachloride in quantity sufficient to form the chloride, $RSO_2Cl.COCl$, while with the third acid it was necessary to use phosphoric pentabromide as the chloride brought about a partial replacement of the bromine on the furfurane ring by chlorine. The chloride (or bromide) was then treated with ammonic hydrate, but instead of obtaining the sulphinide, $RCONHSO_2$, as happens in the benzol group, the result was in every case a diamide. β-Sulphamido-δ-methylpyromucamide,

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[1] The experimental work of this research was carried on under Professor Hill's supervision several years ago, but it has been prepared for publication since his untimely death. The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by J. P. Sylvester. C. L. J.

[2] Remsen and Fahlberg: This JOURNAL, **1**, 426.

[3] Remsen and Fahlberg: *Ibid.*, **1**, 437.

[4] Hill and Jennings: *Ibid.*, **15**, 174 (1893).

[5] Hill and Hendrixson: *Ibid.*, **15**, 151 (1893).

$$C_4HOCH_3.SO_2NH_2.CONH_2,$$

melts at 196° to 197°. β-Sulphamido-δ-chlorpyromucamide,

$$C_4HOCl.SO_2NH_2.CONH_2,$$

melts at 212°. β-Sulphamido-δ-brompyromucamide,

$$C_4HOBr.SO_2NH_2.CONH_2,$$

melts at 219° to 220°.

With a solution of baric hydrate these diamides give off ammonia even in the cold, but instead of the sulphinide hoped for, a β-sulphamidopyromucic acid is formed, and the acids thus obtained did not pass easily into the sulphinides like the corresponding orthosulphamidobenzoic acids. On the contrary, they remained essentially unaltered even when heated alone, or with hydrochloric acid, or oxalic acid. Sulphuric acid had no action in the cold, but charred the substance when hot. The result of our experiments, therefore, is that sulphinides of the furfurane group are not formed under conditions which produce them in the benzol group. Whether they can be made under any conditions must be left to future experiments to decide.

The β-sulphamido-δ-methylpyromucic acid,

$$C_4HOCH_3.SO_2NH_2.COOH,$$

melts at 217° to 218°. The β-sulphamido-δ-chlorpyromucic acid,

$$C_4HOCl.SO_2NH_2.COOH,$$

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[1] Hill and Sanger: Proc. Am. Acad. Sci., **21**, 138; Ann. Chem. (Liebig), **232**, 42.

melts at 194° to 195°. The β-sulphamido-δ-brompyromucic acid,

$$C_4HOBr.SO_2NH_2.COOH,$$

melts at 190° to 191°. Several salts of each of these acids are described. In making the methyl acid the preparation runs essentially without secondary products, but with the chlor- and bromacids a few per cent of the diamide are decomposed with destruction of the furfurane ring.

The action of bromine and water on these sulphamidopyromucic acids gave the following substituted furfuranes:

$C_4HOCH_3Br.SO_2NH_2$, melting-point 123°;
$C_4HOClBr.SO_2NH_2$, melting-point 134° to 135°;
$C_4HOBr_2.SO_2NH_2$, melting-point 153° to 154°.

Further treatment of these substances with bromine and water gave from the methyl compound sulphoacetacrylic acid,

$$CH_3COCHC.COOH.SO_3H,$$

from the two halogen compounds sulphofumaric acid,

$$C_2H.SO_3H(COOH)_2.$$

EXPERIMENTAL PART.

Derivatives of δ-Methylpyromucic Acid.

The pure methylfurfurol needed for the preparation of methylpyromucic acid was obtained by fractional distillation of a large number of impure samples of the oil boiling higher than furfurol obtained from the distillation of wood. The chief impurities were furfurol, and, in much smaller amount, the high-boiling constituents of the crude furfurol oil.

In the preparation of the acid through the oxidation of methylfurfurol by means of argentic oxide, the method described by Sawyer[1] and one of us was followed essentially. It was found, however, that it was not necessary to wash the argentic oxide used in the reaction. One hundred and ten grams of argentic nitrate, giving 75 grams of argentic oxide, were freshly precipitated by means of sodic hydrate in a two-liter flask, the precipitate allowed to settle, and the solution of sodic nitrate decanted. This decantation was found necessary to prevent the serious bumping which occurred if all the sodic nitrate was left in solution and boiled in the oxidation-flask. To the argentic oxide were then added about 15 grams of sodic hydrate dissolved in 1 liter of water. It was found advisable thus to increase the amount of alkali, as if 11 grams, the amount theoretically necessary to form the sodium salt with all the acid produced, were used, some silver was found in solution after filtration. Thirty grams of methyl furfurol were now introduced, and the contents of the flask boiled for thirty minutes with a return-condenser. The sodium salt was then filtered and the methylpyromucic acid separated by means of hydrochloric acid. The yield varied from 88 to 94 per cent. As the acid was somewhat dark in color, it seemed advisable to purify it by the method suggested by Jennings and one of us[1] before converting it into the sulphonic acid. From all samples, therefore, the calcium salt was prepared, a dilute solution of which was boiled for some time with bone-black and then acidified. After this treatment the acid was almost pure white and melted at 107° to 108°, indicating a sufficient degree of purity for the purpose at hand.

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[1] This JOURNAL, 20, 171.

Jennings[2] and one of us have described and analyzed the barium salt of sulphomethylpyromucic acid. This method of preparing the salt was followed. Methylpyromucic acid was slowly added to three times its weight of fuming sulphuric acid while the mixture was well stirred and cooled. The viscous solution was allowed to stand twenty-four hours, then largely diluted with water and neutralized with baric carbonate. The aqueous solution of the barium salt of the sulphonic acid was filtered from the baric sulphate and excess of carbonate. Since the potassium salt was desired as a starting point for further work, the barium was precipitated with potassic carbonate and the filtered solution evaporated to small volume, when, upon cooling, the potassium salt crystallized out. The salt thus obtained was almost white, but was purified for the following work by a single recrystallization from hot water. The amount of potassium salt thus prepared from methylpyromucic acid was from 70 to 80 per cent of the theoretical yield. As this salt has never been described, a small amount of it was purified for analysis by three further recrystallizations from water.

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[1] This Journal, **15**, 167 (1893).

[2] *Ibid.*, **15**, 175 (1893).

Potassic Sulphomethylpyromucate, $K_2C_6H_4SO_6.2H_2O$.—The salt is very readily soluble even in cold water, and its solubility is somewhat increased by heat. It crystallizes in prisms, usually long and slender, the opposite sides of which are parallel. The ends are not quite rectangular. The air-dried salt contains 2 molecules of water and begins to effloresce slowly over sulphuric acid. Heated to 130°, the salt becomes anhydrous very quickly. The determination of the potassium was not a very easy matter. It was found difficult to decompose the salt by means of nitric acid, sulphuric acid, or a mixture of the two without loss by spattering. Finally, however, the analysis was carried through successfully by oxidizing the salt with a comparatively large amount of nitric acid, 6 or 7 cc., and applying heat very slowly and gradually. The nitric acid was followed by sulphuric acid and the potassium weighed as sulphate, as usual.

I. 1.6032 grams air-dried salt lost, at 130°, 0.1814 gram H_2O.

II. 1.3739 grams air-dried salt lost, at 130°, 0.1555 gram H_2O.

	Calculated for $K_2C_6H_4SO_6.2H_2O$.	Found. I.	Found. II.
H_2O	11.30	11.31	11.31

I. 0.5951 gram salt, dried at 130°, gave 0.3661 gram K_2SO_4.

II. 0.6201 gram salt, dried at 130°, gave 0.3800 gram K_2SO_4.

	Calculated for $K_2C_6H_4SO_6$.	Found. I.	Found. II.
K	27.72	27.62	27.51

β-Sulphamido-δ-methylpyromucamide.

Ten grams of anhydrous potassic sulphomethylpyromucate were powdered and placed in a small boiling-flask. To this was added finely divided phosphoric pentachloride in the proportion of 1 molecule of each, and the two substances were well mixed by shaking. The reaction began at once with a slow evolution of heat and partial liquefaction of the contents of the flask. The flask was then placed in an oil-bath and heat gradually applied till the temperature of the bath reached 160°, at which point the temperature was kept from two to three hours. At most, only a few drops of phosphoric oxychloride distilled off. On one occasion, instead of heating at 160°, the bath remained at 120° for half an hour, and the flask stood in a desiccator over night. Under these conditions, also, the reaction was complete; and the yield and purity of the final amido product were the same as in cases where the phosphoric pentachloride was allowed to react at the higher temperature. The treatment of the double acid chloride formed was the same in all cases. The flask was cooled and the viscous contents shaken out into a beaker containing about 100 cc. of cold water. The oily chloride, together with the potassic phosphate and chloride, were well stirred until the potassium salts had dissolved. The emulsion thus formed was poured into a separating-funnel, allowed to settle, and further washed by shaking several times with cold water, which could be done with impunity as the double chloride did not seem particularly reactive with water at 10° to 15°.

The washed chloride was slowly poured, drop by drop, into the strongest ammonic hydrate, which was vigorously stirred and cooled to a temperature of about 10° during the progress of the reaction. The addition of the chloride usually required about an hour; if too much were added at one time, the heat developed was sufficient to cause an ebullition on the bottom of the beaker, which was found to indicate that the reaction was going too fast, and that if not retarded by cooling and stirring, a dark product and low yield would result. If the temperature were in the neighborhood of 0° the reaction proceeded very slowly. After all the chloride had been added, the beaker containing the ammoniacal solution was allowed to stand at the temperature of the room for twenty-four hours. By the end of this time a large part of the ammonia had evaporated, and more or less of the double amide had crystallized out. The solution was heated on the steam-bath until all the ammonia was gone. Then hot water was added, if necessary, in sufficient quantity to dissolve all the amide, the solution cooled, and the crystals separated from the mother-liquor by filtration. The weight of sulphamidomethylpyromucamide obtained varied from 80 to 85 per cent of the theoretical yield. It melted only 1° or so below the melting-point of the pure substance, yet it was invariably somewhat dark in color. This color we failed to remove completely by repeated crystallizations from water, but boiling a solution of the original product with bone-black yielded a substance which was perfectly white. A small amount of the pure white amide was recrystallized from water several times to purify it for analysis. After the first recrystallization the melting-point was not raised, nor was it changed if alcohol were used as a solvent. The substance was evidently pure and was therefore analyzed with the following results:

I. 0.1998 gram substance gave, on combustion, 0.2569 gram CO_2 and 0.0743 gram H_2O.

II. 0.1915 gram substance gave 0.2457 gram CO_2 and 0.0694 gram H_2O.

III. 0.2114 gram substance gave 0.2431 gram $BaSO_4$.

IV. 0.2131 gram substance gave 0.2453 gram $BaSO_4$.

	Calculated for $C_6H_8N_2SO_4$.	Found.			
		I.	II.	III.	IV.
C	35.27	35.06	35.00	....	....
H	3.95	4.16	4.05	....	....
S	15.70	....	....	15.79	15.82

β-Sulphamido-δ-methylpyromucamide.—This substance melts at 196° to 197°. It is very readily soluble in hot water, sparingly in cold. Its aqueous solution is neutral to litmus. Alcohol dissolves it easily, but the solvent power does not change with heat so much as is the case with water. It is insoluble in ether, carbon disulphide, or benzol, and very sparingly soluble in chloroform. From a hot aqueous solution it crystallizes in obliquely terminated prisms which are usually clustered and long and slender. Sometimes, however, they form single and somewhat broader prisms.

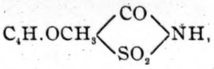
If the phosphoric pentachloride acts normally, a substance like potassic sulphomethylpyromucate would theoretically require 2 molecules of pentachloride for each molecule of the salt. It has been found, however, as stated above, that 1 molecule of phosphoric pentachloride forms a chloride which, after treatment with ammonia, yields 80 to 85 per cent of the theoretical amount of amide. Taking into account the mechanical losses due to washing and separating the oily chloride, and the amount of amide in the mother-liquor, this yield shows that the formation of the double chloride from the potassium salt must have been nearly quantitative, which can be explained by supposing that the phosphoric oxychloride took part in the reaction.

As it seemed of interest to see what effect an additional molecule of phosphoric pentachloride would have, twice the usual amount was tried. In this case a considerable quantity of phosphoric oxychloride distilled over, the thermometer in its vapor reading 107°, while the bath was 160°. In the treatment of the oil with water more heat was developed, and the oil and the amide were darker than usual, but the percentage yield was exactly the same as in the previous preparations. Obviously, then, there was nothing to be gained by using 2 molecules of phosphoric pentachloride.

The acid chloride, which is the product of the phosphoric pentachloride reaction, is a heavy, viscous oil, which did not solidify at 0°. It was not purified except by washing with water, as described above, and was not analyzed. In all cases it was converted immediately into the amide, which has the following formula :

$$C_4HOCH_3.SO_2NH_2.CONH_2.$$

This product is of interest because it brings out a difference in behavior between corresponding compounds of the benzol and furfurane series. Under similar treatment sulphobenzoic acid yields benzoic sulphinide, consequently the substance expected was



$$C_4H.OCH_3{<}\begin{matrix}CO\\SO_2\end{matrix}{>}NH,$$

which differs from the product obtained by 1 molecule of ammonia

β-Sulphamido-δ-methylpyromucic Acid.

When treated with solutions of alkalies, the double amide gave off ammonia even in the cold, and this result was obtained also with baric hydrate. To determine whether all the nitrogen was removed, or if not, what was the acid from which the salt was formed, the following experiment was tried: Four and three-tenths grams of the double amide were placed in a flask and boiled for four hours with baric hydrate, dissolved in 200 cc. of water in the proportion of about 2 molecules of hydrate for each of the amide; at the end of this time no more ammonia was evolved. To collect the ammonia given off, the condenser was connected by a delivery-tube with another flask containing water, and the amount of the ammonia given off was approximately determined at the end of the reaction by titrating the contents of this second flask with a standard hydrochloric acid solution. In this way the presence of 0.366 gram of ammonia was shown, while the amount calculated for 1 molecule was 0.358 gram. The excess of barium was precipitated with carbonic dioxide, and the filtered solution evaporated to a rather small volume. On cooling, 4.6 grams of a crystalline substance were deposited. Qualitative tests showed this to be the barium salt of an acid containing nitrogen and sulphur. The barium was precipitated by sulphuric acid, and the filtrate, upon evaporation, yielded crystals which caused effervescence with carbonates, gave a solution strongly acid to litmus, and melted some 20° higher than the original amide. They, too, contained nitrogen and sulphur and, therefore, were either the sulphamido acid or its anhydride, the sulphinide. Accordingly, more of this acid was prepared from the amide in a similar manner except that the boiling with baric hydrate solution took place in an open flask, which shortened somewhat the time necessary to expel all the ammonia. The yield was satisfactory, as 65 per cent of the theoretical amount of this acid was usually obtained starting from potassic sulphomethylpyromucate. The barium salt was often somewhat colored, and was purified before making the acid, sometimes by the use of boneblack, which was moderately effective, and sometimes by simple recrystallization. The sample of acid used for analysis was made from a barium salt recrystallized four times. The acid itself was then submitted to several crystallizations from water. Further recrystallization of a small amount failed to alter the melting-point. The substance was therefore dried *in vacuo* and analyzed.

I. 0.2205 gram substance gave, on combustion, 0.2823 gram CO_2 and 0.0748 gram H_2O.

II. 0.2198 gram substance gave 0.2818 gram CO_2 and 0.0738 gram H_2O.

	Calculated for		Found.	
	$C_6H_7NSO_5$. I.	$C_6H_5NSO_4$. II.	I.	II.
C	35.10	38.48	34.92	34.96
H	3.44	2.69	3.79	3.76

These analyses made it perfectly evident that the body in question was sulphamidomethylpyromucic acid, I., and not its anhydride, II.

β-Sulphamido-δ-methylpyromucic Acid. — This substance melts at 217° to 218°, and is readily soluble even in cold water. From a hot aqueous solution it crystallizes generally in clusters of long, slender, rectangular prisms. Occasionally these prisms are broadened and shortened, until at times they appear almost cubical. The acid is distinctly more soluble in cold alcohol than in water. It is insoluble in benzol, carbonic disulphide, or chloroform, while in ether it dissolves with difficulty.

In order to learn whether there was any tendency for this acid to form the anhydride, it was submitted to several different treatments favorable to dehydration. 2.5013 grams air-dried acid lost nothing in a desiccator over sulphuric acid for five days. 2.0442 grams acid, dried over sulphuric acid, lost only 0.0007 gram in four hours at 100°, and only 0.0012 gram more when heated four hours at 160°. Of course, this total loss of 0.09 per cent is insignificant.

0.1123 gram was placed in a small test-tube and heated in an oil-bath at a temperature a few degrees above the melting-point of the substance for half an hour. The test-tube was allowed to cool in a desiccator and weighed. The acid lost 0.0097 gram, or 8.64 per cent. The loss calculated for 1 molecule of water is 8.78 per cent. This seemed encouraging, but further study led to the conclusion that this agreement was merely accidental, and that the loss in weight was due to decomposition, not to the formation of an anhydride, for the substance had blackened very considerably; benzol and chloroform would dissolve nothing, while after treatment with water and filtering from the charred residue, which alone was insoluble, the original acid was deposited in its characteristic crystalline form.

A small amount of the substance dissolved without blackening in about 1 cc. of strong sulphuric acid. At the end of an hour it was poured into twice its volume of water. As nothing separated, the solution was extracted with ether, but the ether extract yielded only a small amount of crystals resembling the original acid, and it was shown by another experiment that the acid in aqueous solution could be extracted with ether to some extent.

In another trial the acid, dissolved in sulphuric acid, was heated to 100° when a lively effervescence of sulphurous dioxide set in, accompanied by intense blackening.

Equally unsuccessful was an attempt to dehydrate it by the use of a stream of dry hydrochloric acid gas at 100° or 120°. The weighed substance in the bottom of a tared test-tube was placed in an oil-bath at the desired temperature, exposed to a stream of dry hydrochloric acid gas, and weighed at intervals. After thirty minutes of this treatment at 100° the loss was insignificant, while at 120°, on the contrary, rapid decomposition ensued.

An attempt was then made to use a method of dehydration, described by Fischer,[1] by means of which he succeeded in dehydrating pseudouric acid in a synthesis of uric acid. Two-tenths gram of sulphamidomethylpyromucic acid was mixed with 2 grams of powdered anhydrous oxalic acid in a small tube and heated in an oil-bath for twenty-five minutes from 155° to 185°, then ten minutes more at 190°. The oxalic acid sublimed in large part, and a small amount of the substance melted in the bottom of the tube. Upon cooling, solvents were tried, with the idea of separating from the mass any anhydride if formed, but neither benzol, chloroform, nor carbonic disulphide gave an extract.

From these different experiments it seems necessary to conclude that sulphamidomethylpyromucic acid shows no tendency to form an anhydride of the sulphinide form.

Baric Sulphamidomethylpyromucate, $Ba(C_6H_6NSO_5)_2.3H_2O$. —This salt was obtained before the free acid, as has been described above. It is readily soluble in hot water, rather sparingly in cold, and crystallizes in prickly, spherical masses like burrs or sea-urchins, made up of very short, fine needles. The air-dried salt contains 3 molecules of water, which are given off very slowly over sulphuric acid. The salt, heated to 160°, becomes anhydrous.

I. 1.4826 grams air-dried salt gave 0.5757 gram $BaSO_4$.

II. 3.6688 grams air-dried salt lost, at 160°, 0.3289 gram H_2O.

III. 2.8468 grams air-dried salt lost, at 160°, 0.2567 gram H_2O.

	Calculated for		Found.	
	$Ba(C_6H_6NSO_5)_2.3H_2O$.	I.	II.	III.
Ba	22.91	22.86	....	....
H_2O	9.02	....	8.97	9.02

I. 0.5205 gram salt, dried at 160°, gave 0.2257 gram $BaSO_4$.

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[1] Ber. d. chem. Ges., 28, 2471.

II. 0.4433 gram salt, dried at 160°, gave 0.1893 gram $BaSO_4$.

	Calculated for $Ba(C_6H_6NSO_5)_2$.	Found. I.	Found. II.
Ba	25.18	25.52	25.13

Calcic Sulphamidomethylpyromucate could not be prepared as a solid, owing to its extraordinary solubility in water. Three and three-tenths grams of sulphamidomethylpyromucic acid were boiled with an excess of calcic carbonate, and the filtered solution evaporated to a volume of from 3 to 4 cc. Although containing 3.5 grams of calcium salt, the solution deposited no crystals even after standing in the cold for twelve hours.

Plumbic Sulphamidomethylpyromucate, $Pb(C_6H_6NSO_5)_2$.—This salt was made by boiling an aqueous solution of the acid with plumbic carbonate. It contained crystal water, but the number of molecules was not determined on account of its extremely rapid efflorescence. Two attempts to dry the salt as rapidly as possible between filter-paper under pressure gave widely varying amounts of crystal water. The salt, moreover, exposed to the air of the room could not be made constant, as it rapidly gained or lost weight with different conditions of temperature and humidity. The salt, dried over sulphuric acid, lost nothing upon being heated to 160°. The solubility of the salt is slight in cold water, but is considerably increased by heat. It crystallizes in clusters of long, slender prisms, which rapidly turn to a powder when exposed to the air. It exhibits a strong tendency to form a basic salt which is practically insoluble in water. For example, it was found impossible to recrystallize the anhydrous salt, as when treated with water it would dissolve but very slightly, a light insoluble substance being formed; yet if a small amount of free acid were added, solution easily took place. The basic salt was also formed, if evaporation was carried too far in crystallizing the salt.

I. 0.7595 gram salt, dried at 160°, gave 0.3737 gram $PbSO_4$.

II. 0.9240 gram salt, dried at 160°, gave 0.4546 gram $PbSO_4$.

	Calculated for $Pb(C_6H_6NSO_5)_2$.	Found. I.	II.
Pb	33.63	33.62	33.61

Argentic Sulphamidomethylpyromucate, $AgC_6H_6NSO_5$.—This salt was prepared by adding the calculated amount of argentic nitrate to the potassium salt of sulphamidomethylpyromucic acid. Both salts were dissolved in a very small amount of hot water and allowed to stand in the dark for twelve hours, at the end of which time an abundance of beautiful clusters of small, thin prisms had been formed. These were filtered, dried by exposure to the air of the room, and were evidently anhydrous, for heated to 100°, the loss in weight was insignificant. It was accompanied, however, with a slight change of color to brown, so that it seemed advisable to carry the heat no higher.

0.6202 gram salt gave 0.3714 gram AgBr.

	Calculated for $AgC_6H_6NSO_5$.	Found.
Ag	34.58	34.40

Potassic Sulphamidomethylpyromucate, $KC_6H_6NSO_5.H_2O$.—This salt was prepared from the calcium salt, above mentioned, by precipitation with potassic carbonate. It is readily soluble in cold water, but the solubility is considerably increased by heat. It crystallizes in long, slender prisms with oblique ends, which contain 1 molecule of water. These show a marked tendency to collect in clusters. The hydrous salt is permanent in the air, but loses water very slowly over sulphuric acid, and becomes anhydrous when heated to 125°, increasing very considerably in volume, so that the heating must not take place in too small a dish. There are not any signs of decomposition accompanying this phenomenon, as the salt, after being heated at 125° for seven hours, was perfectly white, although very light and powdery.

I. 2.6050 grams air-dried salt lost, at 125°, 0.1836 gram H_2O.

II. 2.0205 gram air-dried salt lost, at 125°, 0.1401 gram H_2O.

	Calculated for $KC_6H_6NSO_5.H_2O$.	Found. I.	II.
H_2O	6.89	7.05	6.93

I. 0.8319 gram salt, dried at 125°, gave 0.2935 gram K_2SO_4.

II. 0.6045 gram salt, dried at 125°, gave 0.2154 gram K_2SO_4.

	Calculated for $KC_6H_6NSO_5$.	Found. I.	II.
K	16.09	15.85	16.00

ACTION OF BROMINE.

β-Sulphamido-δ-methylbromfurfurane.

Bromine readily oxidizes a cold aqueous solution of any of the salts of sulphamidomethylpyromucic acid with the evolution of carbonic dioxide. The principal product of the reaction varies with the amount of bromine used; with 1 molecule it is sulphamidomethylbromfurfurane, and the reaction is expressed as follows:

$$CH_3.SO_2NH_2.C_4HOCOOK + Br_2 = CH_3.SO_2NH_2.C_4HBrO + KBr + CO_2.$$

For the preparation of this furfurane compound a cold saturated solution of the barium salt was placed in a small flask, and by means of a pump a slow current of air was drawn first through the calculated amount of bromine, and then into the solution. The speed of the stream carrying the bromine vapor was regulated to a considerable degree by the rapidity with which the color of the bromine was bleached by the solution. Two or three hours generally elapsed before the whole was added, and during this time the absorption of the bromine was watched and made as complete as possible by frequently shaking the flask and retarding the air stream if necessary.

No baric sulphate was formed, as was to be expected, from what is already known concerning the behavior of bromine toward substituted sulphopyromucic acids, since work done by one of us with Palmer,[1] Hendrixson,[2] and Jennings[3] has shown that the sulpho group is retained, when bromine and water act on β-sulphopyromucic acids, but that sulphuric acid is formed from δ-sulphopyromucic acids under these conditions.

Before a very large part of the bromine had been added the sulphamidomethylbromfurfurane, which is sparingly soluble in cold water, began to crystallize out of the solution, and when all the bromine had been added this crystalline precipitate was filtered from the mother-liquor. The yields obtained in preparing this substance were rather low, being usually about 50 per cent of the theoretical amount. The product obtained, however, was very pure, often snow-white, with the correct melting-point without recrystallization, and always possessing less color than the salt from which it was made. In preparing a sample for analysis the first product melted at 123°. This was recrystallized twice from water without altering the melting-point. (The substance often melted under water before dissolving, but came out of solution in solid form.) A small amount of the substance was then recrystallized twice from chloroform, but the melting-ing-point was not changed. Analyses gave the following results:

I. 0.2229 gram substance gave, on combustion, 0.2025 gram CO_2 and 0.0563 gram H_2O.

II. 0.2445 gram substance gave, by the Carius method, 0.1917 gram AgBr and 0.2451 gram $BaSO_4$.

III. 0.2305 gram substance gave 0.1806 gram AgBr and 0.2285 gram $BaSO_4$.

	Calculated for $C_5H_6NBrSO_3$.	Found. I.	II.	III.
C	25.00	24.78	....	....
H	2.52	2.82	....	....
Br	33.30	....	33.36	33.34
S	13.35	....	13.77	13.61

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[1] This JOURNAL, **10**, 413 (1888).

Ibid., **15**, 156 (1893).

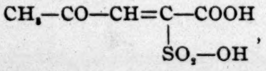
[3] *Ibid.*, **15**, 175 (1893).

β-Sulphamido-δ-methylbromfurfurane melts at 123°. It is sparingly soluble in cold water, much more readily in hot, and is a beautifully crystalline substance. If a hot aqueous solution is cooled rapidly, the substance separates in broad prisms with blunt pointed ends, often in clusters. If the solution is allowed to cool slowly these prisms are very much increased in length. It is easy, by allowing a hot saturated solution to cool even in a 5-centimeter watch-glass, to obtain this substance in very fine needles from 1 to 2 cm. long. In cold alcohol this furfurane compound is extremely soluble, yet it is possible to obtain crystals from an alcoholic solution which are very different from those just described, as they are short, irregular prisms, sometimes almost cubes. It is sparingly soluble in cold benzol, or chloroform, but its solution is considerably increased by heat. In the case of ether, heat makes l ittledifference ; it is readily soluble in it hot or cold. In carbonic disulphide it dissolves with great difficulty. An aqueous solution of sulphamidomethylbromfurfurane is neutral to litmus, and does not decompose carbonates, yet the substance dissolves with great ease in cold, dilute, sodic or potassic hydrate solutions, although sparingly soluble in cold water. No ammonia is given off from such solutions even on boiling, and mineral acids reprecipitate the original substance. In a rough quantitative experiment, over 75 per cent of the compound used was precipitated by dilute sulphuric acid after five hours' boiling with a 15 per cent sodic hydrate solution. This behavior indicated that sulphamidomethylbromfurfurane possessed the properties of a weak acid, and must be capable of forming salts.

To a small amount of the furfurane compound, dissolved in cold alcohol, was added a standardized alcoholic potash solution in the proportion of 1 molecule of each substance. In the course of a few seconds a crystalline precipitate appeared, and after standing a short time this was filtered out and dried by pressure between filter-paper. This body contained potassium and was extremely soluble in water, so much so that it could not be recrystallized from an aqueous solution, nor was it precipitated by the addition of alcohol. From hot absolute alcohol it crystallized in irregular, leafy plates. To an aqueous solution of this potassium salt was added a solution of argentic nitrate, when the silver salt separated as a white, curdy precipitate, which proved to be practically insoluble in water. On account of lack of time, a more complete investigation of the salts of this furfurane compound could not be made. That the hydrogen in the sulphamido group is replaced by metal there can be little doubt, as analogous bodies have been described by Jackson and Wing[1] and Wolkow.[2] Potassic permanganate rapidly oxidizes sulphamidomethylbromfurfurane even in the cold, but as yet the products of the reaction have not been identified.

Action of Bromine on Methylsulphamidobromfurfurane or Action of Bromine in Excess on Salts of Sulphamidomethylpyromucic Acid.

As stated above, when a salt of sulphamidomethylpyromucic acid is treated with aqueous bromine, the product obtained depends upon the amount of bromine used. The furfurane compound just described is easily attacked by bromine, so that if a sufficient amount is added, this first product is decomposed and only the results of more complete oxidation obtained. Although the products of this secondary reaction have been examined only in a qualitative way, little doubt is left concerning what takes place. No sulphuric acid is formed even on boiling. If, however, the acid solution be boiled until the carbonic dioxide is expelled, and baric hydrate then added, a heavy, flocculent precipitate is thrown down which is soluble in hydrochloric acid and reprecipitated by ammonia. This is undoubtedly the barium salt of sulphoacetacrylic acid,



$$CH_3{-}CO{-}CH{=}\underset{\displaystyle SO_2{-}OH}{\underset{|}{C}}{-}COOH,$$

since, under similar conditions, Palmer and one of us,[3] working with δ-brompyromucic acid, obtained baric sulphofumarate. That the NH_2 group is eliminated is shown by the fact that ammonic bromide is found in quantity in the filtrate from the insoluble barium salt. It is probable, moreover, that the oxidation does not stop with the acetacrylic derivative, as was shown by the following experiment: A small amount of bromine was quickly weighed in a tared test-tube partly full of water, and to this was added a quantity of sulphamidomethylpyromucic acid (neutralized with sodic carbonate), such that there would be 2 molecules of bromine to each molecule of the acid. Immediately after mixing, the contents of the tube were well shaken, when there was an immediate heavy precipitate of the bromfurfurane compound, which later did not dissolve completely. The color of the solution in ten seconds became faint yellow and in ten minutes had entirely disappeared. At the end of an hour there was obtained by filtration from the solution 30 per cent of the amount of sulphamidomethylbromfurfurane, which should be obtained theoretically from the weight of acid used, under the best conditions, that is with 1 molecule of bromine.

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[1] This JOURNAL, 9, 340 (1887).

[2] Ztschr. für Chem., 1870, 323.

[3] This JOURNAL, 10, 414 (1888).

It follows from this, as there was so much unoxidized furfurane compound that the bromine must attack the acetacrylic derivative to a certain extent. On the other hand, although there was, as just shown, a considerable amount of the furfurane body left unaltered after 2 molecules of bromine had been absorbed, yet in the earlier experiments, before 1 molecule had been introduced by the slow air-stream, acetacrylic acid was formed, and at the end of the preparations, in which 1 molecule of bromine had been used, a considerable amount of acetacrylic acid was always present. This fact, of course, is one reason for a low yield.

From the above it is seen that this action of bromine upon salts of sulphamidomethylpyromucic acid consists by no means in the conversion of all the acid into the furfurane body, and then of this latter into sulphoacetacrylic acid, and finally of the oxidation of this compound, but rather, that all three of these reactions are to a certain extent progressing at the same time. On account of these facts, in preparing the bromfurfurane, it was convenient, after a large part of the bromine had been added, to filter and observe the action of more bromine on the filtrate.

Derivatives of δ-Monochlorpyromucic Acid.

After the completion of the work already described on derivatives of methylpyromucic acid, it seemed desirable to investigate the behavior of other substituted pyromucic acids under similar treatment. For this purpose the preparation of δ-chlorpyromucic acid, and from it of β-sulpho-δ-chlorpyromucic acid was next undertaken. The monochlor derivative was made according to the method of L. L. Jackson and one of us.[1] Dry pyromucic acid was dissolved in a flask in one and two-thirds times its weight of absolute alcohol, and to this solution was added a quantity of sulphuric acid (sp. gr. 1.84) equal in weight to that of the pyromucic acid used. After heating for four hours on the steam-bath, the mixture was well cooled and then diluted with five or six times its volume of ice-cold water. The oil which separated was thoroughly washed, first with dilute sodic carbonate solution and then with water, cooled until it crystallized, filtered, and dried by exposure to the air. This crude ester was then distilled before treatment with chlorine. The yield of distilled ester amounted to from 94 to 97 per cent of the weight of acid used. This is an increase of over 10 per cent on the yield which Jackson and one of us obtained. The cause of this was the use of ice-water for the dilution of the alcoholic solution, and also the fact that the solution was well cooled with ice during the washing process and before the filtration of the crystallized ester. Proof of this was obtained by cooling with ice a solution filtered at a higher temperature, when an additional amount of ester was precipitated.

For the formation of the chlor acid, the ester was melted in a small tared flask and heated to 145° by means of an oil-bath. Through the melted ester was passed a stream of dry chlorine. The flask containing the ester was weighed from time to time and the process continued until the ester had absorbed 30 per cent of its weight of chlorine. After cooling, it was then slowly poured into three or four times its weight of a very concentrated alcoholic solution of sodic hydrate, the mixture cooled, well stirred, and after standing several hours the sparingly soluble sodic chlorpyromucate was filtered off. To recover the small amount of sodium salt in solution, the filtrate was saturated with carbonic dioxide, the sodic carbonate removed, and the alcoholic solution evaporated to dryness. This, together with the main portion of sodium salt, was dissolved in hot water and the δ-chlorpyromucic acid precipitated by hydrochloric acid.

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[1] This JOURNAL, 12, 26 (1890).

This crude acid melted at about 165°, did not crystallize in the characteristic leafy form, and therefore contained undoubtedly other chlorpyromucic acids, from which it was separated by a method proposed by L. L. Jackson and one of us,[1] depending upon the fact that baric δ-chlorpyromucate is much more soluble than the barium salts of the other chlorpyromucic acids. The volume of water necessary to keep in solution the baric δ-chlorpyromucate formed, and that necessary to prevent after acidification the precipitation of the small amount of dichlor acids left in the filtrate, was readily calculated from the solubility determinations made by Jackson and one of us. The crude acid was suspended in water, neutralized with ammonia, and the solution of the ammonium salt diluted to twelve times the weight of the acid taken. One-quarter of its weight of crystallized baric chloride was then added, the mixture well stirred, and the sides of the beaker scratched with a rod. After the beaker had stood twenty-four hours, the sparingly soluble barium salts, which had precipitated, were removed by filtration, and the solution was diluted with 25 per cent of its volume of water, heated to boiling, and the chlorpyromucic acid precipitated by acidification. The acid thus obtained, although melting at 168°—8° below the proper melting-point—crystallized in the characteristic leafy plates which showed that it contained but a slight amount of impurity. From 275 grams of ester there were obtained 136.8 grams of acid, or 48 per cent of the theoretical amount. A little of the acid, twice recrystallized from benzol, melted at 176°, the melting-point of pure δ-chlorpyromucic acid. For the preparation of the sulphonic acid, however, it was not thought necessary to recrystallize the whole amount.

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[1] This JOURNAL, 12, 27 (1890).

β-Sulpho-δ-chlorpyromucic acid was prepared as described by Hendrixson and one of us.[1] δ-Chlorpyromucic acid was slowly added to four times its weight of fuming sulphuric acid, the mixture being well stirred and cooled. It dissolved more quickly and with less evolution of heat than methylpyromucic acid, and the solution was much lighter colored in this case. The mixture was allowed to stand in a desiccator twenty-four hours, then largely diluted with water and neutralized with baric carbonate, the excess of which, together with the baric sulphate, was removed by filtration. The solution of the barium sulphonate was precipitated with potassic carbonate, the baric carbonate removed, and the filtered solution evaporated to very small volume. On cooling this solution, the potassium salt crystallized out, the weight of which amounted to nearly twice that of the chlorpyromucic acid used, or 95 per cent of the theoretical yield.

β-Sulphamido-δ-chlorpyromucamide.

Potassic sulpho-δ-chlorpyromucate is anhydrous.[2] Accordingly, 25 grams of the powdered salt which had stood for some time over sulphuric acid were mixed in a small boiling-flask with a little more than 2 molecules of finely divided phosphoric pentachloride, about 38 grams, the mixing of the two substances being accomplished merely by shaking the flask. Heat was soon developed, and in a short time almost complete liquefaction took place. In order to complete the reaction, however, the flask was heated in an oil-bath at 110° for three hours, after which most of the phosphoric oxychloride was distilled off under diminished pressure, and when the flask had cooled its pasty contents were shaken out into a beaker containing 200 cc. of cold water. The inorganic potassium salts soon dissolved and the oil which separated was washed in a separating-funnel. The phosphoric oxychloride which remained dissolved in the acid chloride was decomposed very slowly by cold water and its complete removal was not attempted, but after several washings the oil was converted directly into the amide by dropping it slowly into a beaker containing 150 cc. of ice-cold strong ammonia, the mixture being well stirred as the reaction progressed. The ammoniacal solution was allowed to stand in a covered beaker twenty-four hours. It was then poured into a shallow crystallizing dish, where it remained until the ammonia had completely evaporated. Hot water was then added to dissolve the solid, the solution cooled, and the amide which crystallized out filtered off. This first product usually contained some ammonic chloride and was somewhat dark-colored, but upon crystallization and treatment with bone-black the salt was colorless and free from ammonic chloride. The weight of sulphamido-δ-chlorpyromucamide thus obtained was about 12 grams, or 65 per cent of the theoretical amount.

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[1] This JOURNAL, **15**, 151 (1893).

[2] *Ibid.*, **15**, 154 (1893).

In the case of the corresponding methyl compound, it will be remembered, 1 molecule of phosphoric pentachloride was used with practically a quantitative yield of the acid chloride. In this case 1 molecule was at first tried, but the low yields of amide obtained, together with the presence of unaltered potassic sulphochlorpyromucate, even after treatment with phosphoric pentachloride for four hours at 160°, showed that conversion of the potassium salt into the chloride was far from complete. Two molecules were therefore used with much better results, as described above. There was another remarkable difference of behavior observed in the preparation of these two amides. In preparing the methyl compound it was not necessary to wait for the complete evaporation of the ammonia before dissolving the amide. After standing twenty-four hours the residual ammonia was expelled by heat, whereas it was found in the case of the chlor compound that such treatment greatly reduced the yield. In one preparation the solution, which had been allowed to stand for some time but which was by no means free from ammonia, was transferred to a flask and immediately boiled with boneblack for some hours, and although this was the customary treatment in the case of the methyl compound, the yield with the chlor acid was less than one-third the usual amount of amide. Complete spontaneous evaporation of the ammonia at the temperature of the room gave the best results.

The product obtained after treatment with boneblack melted at about 211° and retained a slight yellow color. For analysis a few grams were twice recrystallized from water. The amide then melted at 212°. Further recrystallization of a small amount, using alcohol as the solvent, did not alter the melting-point, nor did it remove the trace of color. The analyses gave the following results :

I. 0.2042 gram substance gave, on combustion, 0.1977 gram CO_2 and 0.0487 gram H_2O.

II. 0.2184 gram substance gave 0.2130 gram CO_2 and 0.0471 gram H_2O.

III. 0.1902 gram substance gave, by the Carius method, 0.1194 gram AgCl and 0.1993 gram $BaSO_4$.

IV. 0.2321 gram substance gave 0.2397 gram $BaSO_4$.

	Calculated for $C_5H_5N_2ClSO_4$.	Found.			
		I.	II.	III.	IV.
C	26.72	26.41	26.60	....	....
H	2.24	2.67	2.41	....	....
Cl	15.78	....	....	15.53	....
S	14.27	....	....	14.39	14.18

These analyses show that the compound is a double amide corresponding completely to the methyl compound already described, and not a sulphinide such as would be formed by the parallel reaction in the benzol series.

β-Sulphamido-*δ*-chlorpyromucamide is very sparingly soluble in cold water or cold alcohol, but either of these solvents, boiling, dissolves it readily, water the more freely, still in hot water it is less soluble than the corresponding methyl compound. In chloroform, ether, carbonic disulphide, or benzol the substance is insoluble. From a hot aqueous solution it crystallizes in short, thick prisms, usually with pointed ends, but sometimes rectangular. If the solution is allowed to cool slowly and quietly, the substance is deposited in large clusters of exceedingly short, stout needles. It melts at 212°.

β-Sulphamido-δ-chlorpyromucic Acid.

Ammonia was evolved from this amide even by the action of a cold solution of baric hydrate, but as the action was slow in the cold, the experiments were carried on at the boiling-point. A cold, saturated solution of baric hydrate was mixed with a quantity of the amide in sufficient volume to give 3 molecules of baric hydrate to each molecule of the amide, and the solution was boiled for two or three hours, at the end of which time the amount of ammonia evolved from the solution had become very slight, and this seemed the best point for stopping the action as it was found that a boiling baric hydrate solution also decomposes the sulphamido group together with the furfurane ring, although only to a limited extent. That such a decomposition of the ring was taking place was shown by the formation of a precipitate in the solution as the boiling continued, which was proved to consist of baric sulphite, carbonate, and oxalate. In order to learn to what extent this total destruction of the molecule took place, this precipitate was filtered out, washed, and then treated in a flask with very dilute hydrochloric acid and bromine, with due care that no sulphurous dioxide should escape. From the weight of baric sulphate obtained it was calculated that about 6 per cent of the amide was usually totally destroyed. This same decomposition was shown to take place when β-sulpho-δ-chlorpyromucate was boiled with baric hydrate, and was apparently more rapid in this case than with the sulphamide. After seventeen hours' boiling with 3 molecules of baric hydrate, 5 grams of this barium salt gave, after the treatment described above, 1.86 grams of baric sulphate, which showed that 71 per cent of the salt had been entirely decomposed. The filtrate was proved to contain considerable amounts of carbonic dioxide and oxalic acid.

The barium salt, which was the principal product of the action of baric hydrate on the amide, was obtained as in the case of the corresponding methyl compound. The weight of air-dried salt amounted to one and one-fourth times that of the amide used. The loss of nitrogen in the form of ammonia from the double amide during the formation of this body showed that it was the salt either of the sulphinide or the sulphamido acid. A sample of it was recrystallized several times, the barium removed by precipitation with sulphuric acid, and the crystals, which separated upon evaporation of the filtrate, still further purified by recrystallization. Their melting-point was 194°. The substance, which was perfectly white, was dried *in vacuo* and analyzed with the following results:

I. 0.2178 gram substance gave, on combustion, 0.2109 gram CO_2 and 0.0387 gram H_2O.

II. 0.3152 gram substance gave 18.3 cc. moist N at 22° and 743 mm. pressure.[1]

	Calculated for		Found.	
	$C_5H_4NClSO_5$.	$C_5H_2NClSO_4$.	I.	II.
C	26.60	28.91	26.40	....
H	1.79	0.97	1.99	....
N	6.22	6.76	....	6.57

These results prove that the δ-chlor double amide, like the methyl compound, gives with baric hydrate salts of sulphamido-δ-chlorpyromucic acid, not of a sulphinide, like those in the benzol series.

The sample of acid analyzed melted, it has been said, at 194°. A small amount of the substance mixed with solid baric hydrate on a watch-glass and moistened with water gave no ammonia that could be detected with turmeric paper, even after gentle warming and long standing. Yet neither this fact nor the analytic results were considered sufficient proof that it was absolutely free from amide in very small traces, which might affect the melting-point. The case was very different from that of the methyl compound where the amide was much more easily decomposed, and where a large excess of baric hydrate could be used without fear of great reduction of the yield. To find a method for complete purification of the acid was not so easy, since the amide was more insoluble in alcohol or water than the acid and in other common solvents the acid was insoluble. It was found, however, somewhat later, that the potassium salt of this acid, although very soluble in water, was precipitated from a concentrated aqueous solution by alcohol, whereas the amide dissolved in water cannot be precipitated in this way. A sample of the potassium salt, which gave no ammonia with concentrated baric hydrate in the cold, was dissolved in water and precipitated by alcohol. This process was repeated five times. From this purified potassium salt was made the silver salt by precipitation with argentic nitrate, and this silver salt, being sparingly soluble in water, was recrystallized from rather a large volume of it. The free acid was then separated by hydrochloric acid and the melting-point observed. It was 194° to 195°. After this thorough purification there was no possibility of the presence of an impurity of amide. The sample was, however, recrystallized from water several times with no change of the melting-point. The melting-point of the substance used for analysis was consequently only a fraction of 1° low.

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[1] The nitrogen determination given above was made after the usual fashion with a tube filled with cupric oxide. After the analysis was well under way it was noticed that Menschutkin ("Analytical Chemistry," p. 488) states that the use of plumbic chromate is necessary in the case of substances containing sulphur, to prevent the reduction of carbonic dioxide to its monoxide by the sulphurous acid formed. The nitrogen, after it had been measured, was accordingly treated with cuprous chloride, and as this caused no diminution in its volume, this accident had not occurred in this case.

β-Sulphamido-δ-chlorpyromucic acid melts at 194° to 195°, and is readily soluble even in cold water; its solubility, however, is increased by heat. From an aqueous solution it crystallizes in rectangular prisms which are often slender and clustered. It is exceedingly soluble even in cold alcohol. In ether it dissolves with great difficulty. It is practically insoluble in carbonic disulphide, chloroform, or benzol.

Although the methyl acid corresponding to this body had shown no tendency to form a sulphinide, two attempts were made to dehydrate this chlor-substance. 0.2571 gram of the acid was heated in a small tube by means of an oil-bath for half an hour at a temperature of 195° to 197°, that is just above its melting-point. The substance blackened somewhat during this treatment, but crystallized on cooling, and melted only 4° below its original melting-point. Carbonic disulphide, chloroform, or benzol, dissolved mere traces of this product, as they did of the original acid. The loss in weight, due probably to slight decomposition, was only 0.0039 gram, or 19 per cent of the weight of 1 molecule of water. 0.3082 gram of the substance contained in a boat placed in a glass tube was heated by means of an air-bath to 120° for three-quarters of an hour, then to 170° for the same length of time, and during the period of heating a rapid stream of hydrochloric acid was passed through the tube. A loss in weight of 2 milligrams was observed which amounted to only 8 per cent of a molecule of water. The substance had turned slightly gray in color, but its melting-point was unaltered. From this work it is apparent that this acid shows no more tendency to lose water than the methyl derivative already examined.

Baric Sulphamido-δ-chlorpyromucate, $Ba(C_5H_3NClSO_5)_2.3H_2O$.—This salt was obtained, as has been said, by the action of baric hydrate directly upon the sulphamidochlorpyromucic amide. It is sparingly soluble in cold water, readily in hot, and crystallizes from a hot solution in masses of small, fine needles, looking like burrs. The tendency to form these aggregations is so great that it is very difficult with the microscope to see any crystalline form—often nothing but small, round lumps can be seen. Moreover, it is hard to free from mother-liquor the crystals which are obtained from the rapid cooling of a hot solution, as they form a kind of paste from which, even with the pump, it is impossible to remove the liquid. Better results are obtained if the solution is allowed to cool slowly and quietly. The salt containing 3 molecules of water is permanent in the air. It begins to lose weight very slowly over sulphuric acid, but quickly becomes anhydrous when heated to 110°.

I. 3.0054 grams air-dried salt lost, at 110°, 0.2521 gram H_2O.

II. 2.0848 grams air-dried salt lost, at 110°, 0.1759 gram H_2O.

	Calculated for $Ba(C_5H_3NClSO_5)_2.3H_2O$.	Found.	
		I.	II.
H_2O	8.43	8.39	8.44

I. 0.9188 gram salt, dried at 110°, gave 0.3660 gram $BaSO_4$.

II. 0.6999 gram salt, dried at 110°, gave 0.2790 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3NClSO_5)_2$.	Found.	
		I.	II.
Ba	23.43	23.45	23.46

Calcic Sulphamido-δ-chlorpyromucate, $Ca(C_5H_3NClSO_5)_2.6H_2O$(?).—The calcium salt was made by boiling a solution of the acid with calcic carbonate and evaporating the filtrate to very small volume. On cooling and allowing the solution to stand for some time the salt, which is very soluble even in cold water, began to crystallize out. It crystallizes in rectangular prisms, often so short as to appear cubical, which sometimes, strangely enough, have very slightly concave ends. The salt was separated from the mother-liquor by rapid filtration on the pump, and remained in the funnel only two or three minutes, when it was well dried by pressure between filter-paper and immediately pulverized and weighed. The weighed salt, on exposure to the air, lost weight, at first, rapidly. During the first hour and a half 1.8743 grams of the salt lost 0.0603 gram, while in the next six hours the loss was only 0.0006 gram, and after that this rate of loss continued, decreasing somewhat toward the end of the six weeks the experiment lasted. As it would have taken too much time to bring it to a constant weight in the air, it was next tried over sulphuric acid when the rate of loss was somewhat increased, but after a few days the substance was heated and soon became constant in weight at 145°, and, as an analysis showed, anhydrous.

1.8743 grams salt, dried between filter-paper, lost, when heated to 145°, 0.3368 gram H_2O.

	Calculated for $Ca(C_5H_3NClSO_5)_2.6H_2O$.	Found.
H_2O	18.09	17.97

This analysis does not settle the amount of water of crystallization definitely, as it may be that the water lost so rapidly in the first ninety minutes was not water of crystallization but hygroscopic moisture. In that case the salt contains 5 molecules of water.

Calculated.	Found.
15.55	15.25

0.5254 gram salt, dried at 145°, gave 0.1438 gram $CaSO_4$.

	Calculated for $Ca(C_5H_8NClSO_5)_2$.	Found.
Ca	8.18	8.05

Plumbic Sulphamido-δ-chlorpyromucate, $Pb(C_5H_8NClSO_5)_2.H_2O$.—This salt was made by boiling a solution of the acid with an excess of plumbic carbonate, filtering, and evaporating. It is very sparingly soluble in cold water, somewhat more readily in hot, and does not show a tendency to form a basic or insoluble anhydrous salt like the corresponding methyl compound. It crystallizes from a hot aqueous solution if cooled quickly in broad, flat, irregular plates. If the solution cools slowly, however, none of this variety appears, but loose clusters of long, thin prisms are obtained. The hydrous salt was permanent in the air and over sulphuric acid. Heated to 140°, it lost a weight corresponding to 1 molecule of water.

I. 2.8785 grams air-dried salt lost, at 140°, 0.0804 gram H_2O.

II. 3.0959 grams air-dried salt lost, at 140°, 0.0849 gram H_2O.

	Calculated for $Pb(C_5H_8NClSO_5)_2.H_2O$.	Found.	
		I.	II.
H_2O	2.67	2.79	2.74

I. 0.6128 gram salt, dried at 140°, gave 0.2830 gram $PbSO_4$.

II. 0.8652 gram salt, dried at 140°, gave 0.3958 gram $PbSO_4$.

	Calculated for $Pb(C_5H_8NClSO_5)_2$	Found.	
		I.	II.
Pb	31.53	31.53	31.25

Argentic Sulphamido-δ-chlorpyromucate, $AgC_5H_8NClSO_5$.—This salt was made by adding to a hot solution of the potassium salt the calculated amount of argentic nitrate. The salt separated at once. For analysis it was recrystallized from a hot solution. It is sparingly soluble in cold water, more readily in hot, and crystallizes in rectangular prisms and plates, which are usually grouped together in irregularly shaped masses. The air-dried crystals are anhydrous, losing no weight in three hours at 110°.

0.4652 gram air-dried salt gave 0.2006 gram AgCl.

	Calculated for $AgC_5H_3NClSO_5$.	Found.
Ag	32.46	32.46

Potassic Sulphamido-δ-chlorpyromucate, $KC_5H_3NClSO_5$.—This salt was prepared by neutralizing the free acid with potassic carbonate. Although dissolving freely in cold water its solubility is increased by heat. It crystallizes in beautiful rectangular prisms, usually three or four times as long as broad, but sometimes these are shortened into broad plates, and occasionally become perfectly square. They are rarely grouped in clusters. A very insignificant loss in weight took place upon heating the air-dried salt for three hours at 160°. It was evidently, therefore, anhydrous.

I. 0.5617 gram air-dried salt gave 0.1830 gram K_2SO_4.
II. 0.7536 gram air-dried salt gave 0.2452 gram K_2SO_4.

	Calculated for $KC_5H_3NClSO_5$.	Found. I.	Found. II.
K	14.84	14.63	14.61

Considerable difficulty was encountered in oxidizing this salt for analysis without serious loss of substance. Determination (I) was made by dissolving the salt in a mixture of very dilute sulphuric and nitric acids and slow evaporation on the steam-bath, followed by very careful heating with a ring-burner. In analysis (II), the salt was dissolved in water, bromine added to precipitate the furfurane compound (this reaction is described below) and the filtrate, after driving off the excess of bromine, evaporated in platinum, followed by treatment with sulphuric acid in a crucible. This method was no more satisfactory than the first, as the furfurane compound which had been dissolved by the necessary washing showed the same tendency to spatter in burning.

Action of Bromine and Water. β-Sulphamido-α,α-chlorbromfurfurane.

With bromine, salts of sulphamido-δ-chlorpyromucic acid show a behavior similar to that, already described, of the salts of the corresponding methyl acid. With equal molecules of acid and bromine a bromfurfurane compound is obtained with the evolution of carbonic dioxide. Seven grams of anhydrous barium salt were dissolved in water and by means of a slow current of air 3.8 grams of bromine were introduced. No baric sulphate was formed. The crystalline precipitate was filtered from the mother-liquor and amounted to 5.2 grams, or 85 per cent of the theoretical yield. This substance melted at 130° to 131° and contained a small amount of sulphamidochlorpyromucamide, shown by the formation of ammonia with baric hydrate in the cold, but this was due to the fact that a sample of barium salt had been used which was not entirely free from that body. Owing to its insolubility in cold water and rapid increase of solubility with heat, the furfurane compound was purified by two recrystallizations from large volumes of hot water, when it melted at 134° to 135° and contained no amide. This melting-point was not altered by two more crystallizations from hot water and three from chloroform. The analyses gave the following results:

I. 0.2062 gram substance gave, on combustion, 0.1383 gram CO_2 and 0.0303 gram H_2O.

II. 0.2468 gram substance gave, by the Carius method, 0.3145 gram AgCl + AgBr (which yielded 0.4455 gram AgI), and 0.2239 gram $BaSO_4$.

	Calculated for $C_4H_3NClBrSO_3$.	Found. I.	Found. II.
C	18.42	18.29	....
H	1.16	1.64	....
Cl + Br	44.29	....	44.39
Cl	13.61	....	13.57
Br	30.68	....	30.86
S	12.30	....	12.46

After the Carius determination the mixture of argentic chloride and bromide was dissolved from the Gooch mat with a little strong potassic cyanide solution, three or four times the theoretical amount of potassic iodide was added, after which the cyanide was decomposed, and all the silver precipitated as iodide by the addition of dilute sulphuric acid.

β-Sulphamido-α,α-chlorbromfurfurane melts at 134° to 135°. It is sparingly soluble in cold water, readily soluble in hot, and crystallizes from a hot aqueous solution in clusters of long needles even if rapidly cooled in a watch-glass. If a large volume is allowed to cool slowly, magnificent, long needles result. It is extremely soluble even in cold alcohol, and it is with difficulty that crystals can be obtained from an alcoholic solution. Such crystals, however, are very different in appearance from those from the aqueous solution, as they are small, irregular, thick prisms. It is not very soluble in ether, hot or cold. In hot chloroform or benzol it dissolves moderately freely, separating in the form of fine needles as the solution cools. Carbonic disulphide dissolves it but sparingly.

Sulphamidochlorbromfurfurane, like the methyl compound already described, acts as a weak acid, being readily dissolved by cold solutions of the alkalies and precipitated by mineral acids. The potassium salt, which is extremely soluble in water, was prepared by the addition of alcoholic potash to the furfurane compound dissolved in alcohol. After a few minutes the salt crystallized from this solution and was filtered out and recrystallized from absolute alcohol. It separated in shining, irregular scales. An aqueous solution of argentic nitrate was added and the silver salt was precipitated in the form of compact masses of small, fine needles. It is very insoluble even in hot water. These compounds were not analyzed, but they undoubtedly correspond to the salts prepared from the methylfurfurane body and probably have the metal attached to nitrogen in the SO_2NH_2 group.

The formation of sulphamidochlorbromfurfurane from sulphamidochlorpyromucic acid with 1 molecule of bromine corresponds to the behavior of the methyl acid described above, and this similarity also extends to the action with more bromine, as with this the furfurane body in question is oxidized, no sulphuric acid is formed, and baric hydrate, after the expulsion of the carbonic dioxide, gives a heavy, flocculent precipitate soluble in hydrochloric acid and reprecipitated by ammonia. Although this body has not been analyzed, there is no doubt that it is the baric sulphofumarate obtained first by Palmer and one of us[1] and later by Hendrixson and one of us.[2]

Derivatives of δ-Monobrompyromucic Acid.

In making the δ-monobrompyromucic acid the method of preparation given by Sanger and one of us[3] was followed except in a few details. Dry pyromucic acid was treated with the vapor of bromine at 100°. For 20 grams of pyromucic acid a half-liter Erlenmeyer flask was used, provided with a return-condenser and a drop-funnel, the end of which entered the mouth of a test-tube resting upon the bottom of the flask and serving to catch the liquid bromine. The bottom of this test-tube had been blown out and flattened so that more surface would be heated for the volatilization of the liquid, and a large hole had been blown in its side 2 cm. from the bottom, through which the bromine vapor might escape.

The powdered acid, mixed with glass beads in order to present more surface to the action of the bromine, was placed on the bottom of the flask and heated on the steam-bath. For 20 grams of acid 36 grams of bromine were used, and its introduction required about three hours. By the end of two more hours the bromine was completely absorbed; the acid was then dissolved in boiling water, and filtered in a steam-funnel. Upon cooling, the solution deposited about 60 per cent of the theoretical amount of δ-brompyromucic acid. This first product melted at about 177°. In order to free it from dibrompyromucic acids a method was resorted to similar to that employed for the purification of the chlor compound, which depended upon the insolubility of the barium salts of the dibrom acids. The product was dissolved in forty times its weight of water, one-tenth of its weight of baric chloride added, the solution allowed to stand for some time, and the barium salts of the sparingly soluble dibrom acids filtered off. Upon acidification of the filtrate the acid separated in leafy plates which melted at 180°, and was sufficiently pure for the preparation of the sulphonic acid. β-Sulpho-δ-brompyromucic acid and its salts have been made and described by Palmer and one of us.[1] Dry δ-brompyromucic acid was slowly stirred into three and one-half times its weight of fuming sulphuric acid while the beaker containing the mixture was cooled. Solution took place quickly and the amount of color developed was slight, as was the case with the δ-chlor compound. The solution was allowed to stand twenty-four hours before dilution; baric carbonate was then added to neutralization, and the filtered solution precipitated with potassic carbonate. The baric carbonate was filtered off and the solution of the potassium salt evaporated and crystallized. Somewhat over 90 per cent of the theoretical yield of potassium salt was obtained.

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[1] This JOURNAL, **10**, 414 (1888).

[2] *Ibid.*, **15**, 156 (1893).

[3] Proc. Am. Acad., **21**, 138; Ann. Chem. (Liebig), **232**, 42.

β-Sulphamido-δ-brompyromucamide.

It was attempted to prepare sulphamido-δ-brompyromucamide from potassic sulphobrompyromucate by the action of phosphoric pentachloride and ammonia, in the same manner in which the corresponding methyl and chlor compounds had been made. One or two attempts showed that while there was undoubtedly δ-bromamide formed, yet there was also produced in no very small quantity the δ-chlor compound, which has already been described. The presence of potassic bromide in the reaction flask, together with the dark-red color which the acid chloride assumed was enough to prove that part of the bromine in the δ-position on the furfurane ring was set free and replaced by chlorine. The product of the reaction after one recrystallization was tested qualitatively for chlorine. About 0.2 gram of the substance was mixed with sodic carbonate and potassic nitrate, oxidized in a hot crucible, fused with potassic dichromate, and submitted to the chromic oxychloride test for chlorine. More than a trace was present. As it would evidently be a useless task to attempt to purify this bromamide, owing to the similarity of the properties of the two bodies, this method of preparation was abandoned.

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[1] This JOURNAL, 10, 408 (1888).

Phosphorous terbromide was next tried on a small scale with unsatisfactory results. Three molecules of the potassium salt (3 grams) were treated with two of phosphorous terbromide (1.7 grams) for two hours at 130°. After treatment with water an oil separated which, with ammonic hydrate, yielded nothing resembling the expected amide, but instead, 0.7 gram of a light-brown powdery substance, which was practically insoluble in water and melted at 122°. Unfortunately, owing to lack of time, this body could not be investigated.

Attention was then turned to phosphoric pentabromide. This substance was prepared from equal molecules of phosphorous terbromide and bromine. The bromine was allowed to drop slowly from a burette into the terbromide contained in a mortar. The mixture was well stirred at first with a rod and then powdered with a pestle as it became solid. The pentabromide was removed to a bottle and a stream of dry air passed through it to remove any excess of bromine. Thus prepared, the pentabromide remained dry and powdery, and could be weighed out for use with little difficulty. With it satisfactory results were obtained by the following method: The potassium salt was mixed in a dry boiling-flask with a little over 2 molecules of pentabromide and the mixture heated in an oil-bath. At 70° the contents of the flask liquefied. The temperature was kept at 90° from two to three hours, when the flask was allowed to cool, and its dark-red, viscous contents poured into a beaker of cold water. After a vigorous stirring, during which some heat was developed by the decomposition of the phosphoric oxybromide, the beaker was cooled with water, whereupon the oil solidified, and the wash-water was removed by decantation. The bromide was melted and stirred with water at about 30°, then cooled again, and the water decanted from the solid. This washing of the bromide as an oil and decantation of the wash-water after solidification was continued until the solid bromide lost its red color and became light yellow and the wash-waters contained no bromine and only slight amounts of hydrobromic acid.

The treatment of the solid acid bromide with ammonic hydrate resembled in all respects that of the liquid acid chloride of chlorpyromucic acid recently described. The ammonia was ice-cold, small amounts of substance were slowly introduced, the solution was well stirred during the reaction, and then allowed to stand until the ammonia had completely volatilized. Upon treatment with hot water there remained insoluble a small amount of a light-brown substance which resembled the product obtained with phosphorous terbromide. From this the solution was filtered, evaporated, and allowed to cool, when it deposited the amide in crystalline form, the weight of which amounted to 50 per cent of the theoretical yield. The melting-point of this product once recrystallized was 200° to 201°, which was not altered by three recrystallizations from water, but the substance did not fuse sharply. A sample was analyzed with the following results:

I. 0.2072 gram substance gave, on combustion, 0.1697 gram CO_2 and 0.0360 gram H_2O.

II. 0.2713 gram substance gave, by the Carius method, 0.1900 gram AgBr and 0.2372 gram $BaSO_4$.

	Calculated for $C_5H_5N_2BrSO_4$.	Found.	
		I.	II.
C	22.30	22.33	....
H	1.87	1.95	....
Br	29.70	....	29.80
S	11.91	....	12.00

These analytic results show that here too a sulphinide has not been obtained, but that the substance is sulphamidobrompyromucamide. Yet, as the melting-point was not sharp, it must have contained an amount of impurity which could not be detected by analysis, but was sufficient to affect seriously the melting-point.

As the substance melted no more sharply after two more crystallizations from water, alcohol was tried as a solvent, when, after two crystallizations, the substance began to melt at 201°, but was not completely liquefied until the temperature reached 219°. Four more crystallizations from the same solvent gave the melting-point 219° to 220°, which is undoubtedly the fusing-point of the pure substance, since it was not changed by two final crystallizations. The yield of the final purified product was small. There was enough, however, to make a halogen determination.

0.1331 gram substance gave, by the Carius method, 0.0931 gram AgBr.

	Calculated for $C_5H_5N_2BrSO_4$.	Found.
Br	29.70	29.75

β-Sulphamido-δ-brompyromucamide melts at 219° to 220°, and is sparingly soluble in cold water or alcohol; with heat it dissolves readily in these solvents. In ether, chloroform, carbonic disulphide, or benzol it is insoluble. From an aqueous solution quickly cooled it crystallizes in small, short, rectangular prisms. If a dish containing a hot solution is allowed to cool slowly, the crystallized substance presents a peculiar aspect, as it appears in lines of hard, hemispherical lumps, 2 or 3 mm. in diameter, clinging to the glass and radiating from the centre of the dish. Sometimes with the aid of a lens short, thick, spike-like points can be seen projecting from these masses.

Since the compound just described was proved by analysis to be analogous to the chlor and methyl double amides previously investigated, another instance of difference in behavior between benzol and furfurane derivatives had been found.

β-Sulphamido-δ-brompyromucic Acid.

In order to study the behavior of this double amide with baric hydrate, 8.3 grams of amide were boiled in a flask with a solution of baric hydrate in the proportion of 3 molecules of hydrate to each molecule of the amide. The treatment was continued three hours, during which time the formation of a precipitate occurred in the solution, showing decomposition of the furfurane ring, as was the case in the similar treatment of the chlor compound. At the end of the boiling ammonia was slowly evolved, also showing decomposition. The amount of baric sulphite formed was determined as before, and showed total decomposition of 7.5 per cent of the amide. The alkaline solution, after filtration, was treated with carbonic dioxide, again filtered and evaporated, 9 grams of barium salt crystallized from the solution on cooling. This salt gave off no ammonia in one hour with cold baric hydrate and was therefore free from amide. It was, however, thrice recrystallized, the barium precipitated by sulphuric acid, and the crystals of acid obtained from the filtrate purified by recrystallizing them six times from water. After the third time the melting-point remained constant at 190° to 191°. The substance was dried *in vacuo* and analyzed:

I. 0.2560 gram substance gave, on combustion, 0.2057 gram CO_2 and 0.0460 gram H_2O.

II. 0.1560 gram substance gave, by the Carius method, 0.1079 gram AgBr.

	Calculated for		Found.	
	$C_5H_4NBrSO_5$.	$C_5H_2NBrSO_4$.	I.	II.
C	22.21	23.81	21.92	....
H	1.49	0.80	2.01	....
Br	29.59	31.72	....	29.44

These analyses show that the substance is sulphamidobrompyromucic acid and not the sulphinide. The 9 grams of barium salt obtained in the process just described amounted to 80 per cent of the theoretical yield.

β-Sulphamido-δ-brompyromucic acid melts at 190° to 191°. The acid is readily soluble even in cold water, and is extremely soluble in alcohol. It crystallizes in long, thin, rectangular prisms, which usually appear in clusters of slender needles. In ether it is very sparingly soluble, and practically insoluble in chloroform, carbonic disulphide, or benzol.

That it shows no more tendency to form an anhydride than did the corresponding methyl and chlor acids was made evident by the following work: 0.1668 gram of the acid was heated for three-quarters of an hour at 193° to 195°. The substance blackened somewhat, but crystallized on cooling, melted only 4° below the proper melting-point, and the loss in weight of 0.0030 gram corresponded to but 27 per cent of a molecule of water. Chloroform, benzol, or carbonic disulphide dissolved nothing from the residue. The acid was therefore practically unchanged. Heating the substance for two hours at 170° in a rapid current of dry hydrochloric acid gas had a similar effect. The melting-point was lowered 4°, the color of the body changed from pure white to a light gray, and the loss in weight amounted to only 20 per cent of 1 molecule of water.

Baric Sulphamido-δ-brompyromucate, $Ba(C_5H_3NBrSO_5)_2.3H_2O$.—This salt was obtained directly from the amide by the action of baric hydrate, as has been described. It was purified by recrystallization from water. It is very readily soluble in hot water, sparingly in cold. It is deposited from a hot solution in small, round masses of fine needles looking like sea-urchins. The air-dried salt is permanent in the air and contains 3 molecules of water, which begins to escape slowly over sulphuric acid. The salt quickly becomes anhydrous at 130°. It was analyzed with the following results:

I. 3.0575 grams air-dried salt lost, at 130°, 0.2308 gram H_2O.

II. 2.4456 grams air-dried salt lost, at 130°, 0.1838 gram H_2O.

	Calculated for $Ba(C_5H_3NBrSO_5)_2.3H_2O$.	Found.	
		I.	II.
H_2O	7.41	7.55	7.51

I. 0.7015 gram salt, dried at 130°, gave 0.2428 gram $BaSO_4$.

II. 0.6371 gram salt, dried at 130°, gave 0.2206 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3NBrSO_5)_2$.	Found.	
		I.	II.
Ba	20.34	20.37	20.38

The calcium salt, like that of the corresponding methyl acid, was found to be too soluble in water for investigation. A solution of the acid, boiled with calcic carbonate, filtered, and evaporated to very small volume, deposited nothing even after several hours standing.

Plumbic Sulphamido-δ-brompyromucate, $Pb(C_5H_3NBrSO_5)_2.2H_2O$.—This salt was prepared by boiling an aqueous solution of the acid with plumbic carbonate. The filtered solution was evaporated and allowed to cool, whereupon the salt which is sparingly soluble in cold water began to crystallize from the solution. It was deposited in peculiar shuttle-shaped crystals, usually short with pointed ends and curving sides. Occasionally they were longer with straight parallel sides, but the ends, as before, curving and pointed. These crystals often occur in clusters. The air-dried salt was twice obtained for analysis by crystallization, contained 2 molecules of water and was permanent in the air. Once, a salt with less water was obtained, which was probably due to crystallization from solution at a higher temperature. The air-dried salt loses its 2 molecules of water almost completely when placed for a few days over sulphuric acid. A very small additional loss in weight was noted upon heating to 145°.

I. 1.9397 grams air-dried salt lost, over sulphuric acid, 0.0861 gram, and in addition 0.0015 gram at 145°.

II. 1.8167 grams air-dried salt lost, over sulphuric acid, 0.0833 gram, and in addition 0.0003 gram at 145°.

	Calculated for	Found.	
	$Pb(C_5H_3NBrSO_5)_2.2H_2O$.	I.	II.
H_2O	4.61	4.52	4.60

I. 0.5994 gram salt, dried at 145°, gave 0.2433 gram $PbSO_4$.

II. 0.7833 gram salt, dried at 145°, gave 0.3173 gram $PbSO_4$.

	Calculated for	Found.	
	$Pb(C_5H_3NBrSO_5)_2$.	I.	II.
Pb	27.77	27.72	27.67

Argentic Sulphamido-δ-brompyromucate, $AgC_5H_3NBrSO_5.1\frac{1}{2}H_2O$.—The silver salt was prepared by the precipitation of a concentrated solution of the potassium salt with argentic nitrate. The salt was dissolved in hot water, filtered, and recrystallized. It is very sparingly soluble in cold water, but dissolves readily with heat, and crystallizes in short, thick prisms which are not quite rectangular. The air-dried salt, which contains 1.5 molecules of crystal water, is permanent in the air, but over sulphuric acid slowly loses weight, and when heated to 110° quickly becomes anhydrous.

I. 2.2394 grams air-dried salt lost, at 110°, 0.1476 gram H_2O.

II. 1.4611 grams air-dried salt lost, at 110°, 0.978 gram H_2O.

	Calculated for $AgC_5H_3NBrSO_5.1\frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	6.69	6.59	6.69

0.8050 gram salt, dried at 110°, gave 0.4006 gram AgBr.

	Calculated for $AgC_5H_3NBrSO_5$.	Found.
Ag	28.62	28.58

Potassic Sulphamido-δ-brompyromucate, $KC_5H_3NBrSO_5.H_2O$. —The potassium salt was made by the action of potassic carbonate on the solution of the calcium salt described above. The filtered solution was evaporated to very small volume when, upon cooling, the potassium salt crystallized out. It separates from solution in very slender, rectangular prisms, which are almost invariably loosely clustered. The air-dried salt contains 1 molecule of water, which it does not lose over sulphuric acid, but it becomes anhydrous when heated to 160°.

I. 2.3727 grams air-dried salt lost, at 160°, 0.1336 gram H_2O.

II. 1.9753 grams air-dried salt lost, at 160°, 0.1108 gram H_2O.

	Calculated for $KC_5H_3NBrSO_5.H_2O$.	Found.	
		I.	II.
H_2O	5.52	5.63	5.61

I. 0.6731 gram salt, dried at 160°, gave 0.1872 gram K_2SO_4.

II. 0.3930 gram salt, dried at 160°, gave 0.1113 gram K_2SO_4.

	Calculated for $KC_5H_3NBrSO_5$.	Found.	
		I.	II.
K	12.70	12.49	12.71

Action of Bromine and Water. β-Sulphamido-α,α-dibromfurfurane.

The behavior of aqueous bromine with the salts of sulphamido-δ-brompyromucate is entirely analogous to its behavior, already described, with the salts of the corresponding chlor compound. Five grams of anhydrous baric sulphamido-δ-brompyromucate were dissolved in water and treated by means of an air-stream with 2.4 grams of bromine vapor—1 molecule for each furfurane ring. At the end of two hours the addition of the bromine was completed and there were filtered from the solution 3.7 grams of crystalline precipitate. This substance melted at 148° to 150°, and represented 85 per cent of the theoretical yield of the furfurane compound. It was recrystallized three times from about 200 cc. of water. After the first crystallization the melting-point was 153°.5, and neither the last two crystallizations from water nor subsequent trials with benzol or chloroform altered it. An analysis gave the following results:

I. 0.2135 gram substance gave, on combustion, 0.1221 gram CO_2 and 0.0245 gram H_2O.

II. 0.2649 gram substance gave, by the Carius method, 0.3253 gram AgBr.

	Calculated for $C_4H_3NBr_2SO_3$.	Found. I.	II.
C	15.74	15.60	....
H	0.99	1.28	....
Br	52.43	....	52.26

β-Sulphamido-α,α-dibromfurfurane melts at 153°.5. It is very insoluble in cold water, more readily soluble in hot, and crystallizes from a hot solution in very long, thin, obliquely terminated prisms, usually in clusters. The substance is very soluble even in cold alcohol, but crystallizes from a hot solution in small, thick prisms, rather irregular in shape. In ether it is somewhat soluble, and also in hot chloroform, from which it crystallizes, on cooling, in fine needles. In hot benzol it is readily soluble, sparingly in cold. The substance is practically insoluble in carbonic disulphide.

The feeble acid properties of the sulphamido group appear in this compound, and it is readily soluble in alkalies and precipitated by acids. The potassium salt was precipitated by the addition of alcoholic potash to an alcoholic solution of the furfurane body. This salt, recrystallized from absolute alcohol, appeared in beautiful, shining scales. From an aqueous solution of this the crystalline silver salt was precipitated with aqueous argentic nitrate. The potassium salt is extremely soluble in water, the silver salt practically insoluble.

Sulphamidodibromfurfurane was easily oxidized in cold aqueous solution by bromine with the formation of the same sulphofumaric acid which was obtained by the oxidation of the chlorbrom compound. After an excess of bromine had been added and the carbonic dioxide expelled, it was found that sulphuric acid was absent, but that baric hydrate produced the voluminous, flocculent precipitate, characteristic of sulphofumaric acid.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF POTASSIC NITRITE ON MUCOBROMIC ESTER.[1]

BY H. B. HILL AND O. F. BLACK.

The products formed by the action of alkaline nitrites upon mucobromic acid, which were first described by Hill and Sanger[2] in 1882, have been repeatedly the subject of investigation in this laboratory during the past few years.[3] A product of an entirely different nature, which they obtained by the action of potassic nitrite upon ethyl mucobromate, has not been further described. Its formula was shown at the time to be $KC_6H_6NO_6$, but no reactions were discovered which gave definite proof of its structure. A few years later Mr. W. S. Hendrixson made a preliminary study of the body and obtained some interesting results, but he was unable to bring the investigation to a definite conclusion before his departure from Cambridge. We are indebted to him for certain experimental material, which we shall describe later.

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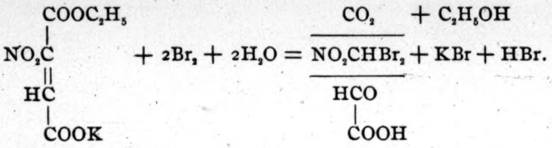
[1] The work described in this paper was done under the supervision of Professor Hill, but the paper was written after his untimely death. C. L. J.

[2] Ber. d. chem. Ges., 15, 1910 (1882).

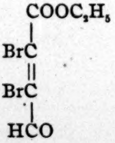
[3] This JOURNAL, 22, 89; 24, 1. Ber. d. chem. Ges., 33, 1241.

The structure of the compound $KC_6H_6NO_6$ was determined by studying the action of bromine and water upon it, which decomposed it, giving an oil identified as dibromnitromethane and glyoxylic acid, which was detected in the aqueous liquid by conversion into its phenylhydrazone identified by analysis. As it was possible that this glyoxylic acid might have proceeded from the oxidation of the ethyl group of the ethyl mucobromate, the experiment was repeated with the corresponding salt, $KC_5H_4NO_6$, made from methyl mucobromate, and, as this also gave glyoxylic acid when treated with bromine and water, it follows that this acid results from a breaking up of the molecule of the new acid. This decomposition proves that the substance is potassic ethylnitromaleate, as shown by the following reaction:

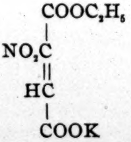


$$\begin{array}{r} \mathrm{COOC_2H_5} \\ | \\ \mathrm{NO_2C} \\ \| \\ \mathrm{HC} \\ | \\ \mathrm{COOK} \end{array} + 2\mathrm{Br_2} + 2\mathrm{H_2O} = \begin{array}{l} \mathrm{CO_2} + \mathrm{C_2H_5OH} \\ \hline \mathrm{NO_2CHBr_2} + \mathrm{KBr} + \mathrm{HBr}. \\ \hline \mathrm{HCO} \\ | \\ \mathrm{COOH} \end{array}$$

The relation of this potassic ethylnitromaleate to the ethyl mucobromate, from which it is formed, is made evident by the following formulas:

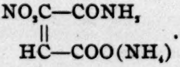


$$\begin{array}{r} \mathrm{COOC_2H_5} \\ | \\ \mathrm{BrC} \\ \| \\ \mathrm{BrC} \\ | \\ \mathrm{HCO} \end{array}$$



$$\begin{array}{r} \mathrm{COOC_2H_5} \\ | \\ \mathrm{NO_2C} \\ \| \\ \mathrm{HC} \\ | \\ \mathrm{COOK} \end{array}$$

The structure thus determined for this compound was confirmed by the study of the action of ammonia upon it, which formed the amide

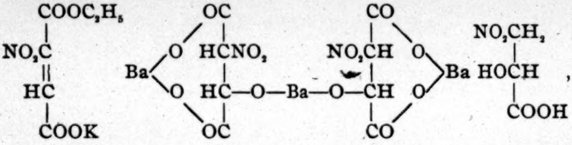


$$\begin{array}{l} \mathrm{NO_2C{-}CONH_2} \\ \;\;\;\;\;\| \\ \;\;\mathrm{HC{-}COO(NH_4)} \end{array}.$$

Several of the salts derived from this amido acid were made and analyzed.

The potassic ethylnitromaleate is, in some respects, a remarkably stable substance, as it was not decomposed even by evaporation to dryness with strong hydrochloric acid, and all attempts to convert it into salts with other metals than potassium failed. We did, however, succeed in making an ammonium and an aniline salt, the latter of which was analyzed.

When the potassic ethylnitromaleate in aqueous solution was treated with baric hydrate a voluminous precipitate was formed, which was not the ethylnitromaleate but the salt of another acid, since the addition of dilute hydrochloric acid decomposed it with evolution of carbonic dioxide and formation of nitrolactic acid. Its formation from the potassic ethylnitromaleate on the one hand, and its conversion into nitrolactic acid on the other, indicate that it is a basic baric nitromalate formed by the addition of water to the nitromaleate,



but the percentage of barium in such a salt is 53.87, whereas our analyses gave results varying from 54.68 to 56.45 per cent of barium. This, however, should not lead to the rejection of this theory, since this excess of barium was undoubtedly caused by the presence of some baric carbonate, which could hardly be avoided in a precipitate formed from baric hydrate with the salt of such an unstable acid and incapable from its nature of purification. Another theory in regard to this salt was that it consisted of a mixture of baric carbonate and baric nitrolactate, which would explain its behavior with acids as well as the theory that it was a nitromalate. To decide between these theories we determined the number of molecules of baric hydrate necessary to form the salt from each molecule of potassic ethylnitromaleate. If it was a mixture of carbonate and nitrolactate 2 molecules would be necessary ; if it was a nitromalate, one and a half. As a matter of fact, 1.635 molecules of baric hydrate were found to be necessary. There is no doubt, therefore, that the salt is the basic baric nitromalate.

Nitrolactic acid (α-oxy-β-nitropropionic acid),

$$H_2CNO_2CHOHCOOH,$$

was formed by the action of dilute hydrochloric acid on the basic baric nitromalate, carbonic dioxide being evolved. The composition of the nitrolactic acid, which melts at 76° to 77°, was determined by its analysis and an analysis of its silver salt. With baric hydrate the nitrolactic acid formed a pinkish-white precipitate, which gave percentages of barium on analysis about 2 per cent too high for the formula

$$(CH_2NO_2CHOCOO)Ba.$$

We ascribe these results to a slight amount of baric carbonate in the precipitate, as in the case of the basic baric nitromalate discussed above, for, although the calculated amount of barium would agree fairly with that found, if we assumed the formation of an anhydride by the removal of 1 molecule of water from two of the basic salt, such an assumption seems inadmissible in this case, because the salt gives unaltered nitrolactic acid on acidification.

The acetnitrolactic acid, $H_2CNO_2HCOC_2H_3OCOOH$, and its silver salt were made and analyzed.

The nitrolactic acid contains an unsymmetrical atom of carbon, and we accordingly studied its action toward polarized light. Our experiments, which did not go beyond the preliminary stage, showed that an active acid could be obtained which showed a specific laevo rotation of about 20°.

The constitution of the nitrolactic acid was determined by reducing it with tin and hydrochloric acid, which converted it into isoserin (β-aminolactic acid), $CH_2NH_2CHOHCOOH$, recognized by its characteristic copper salt,[1] $C_3H_5O_3NCu$, and by a determination of its solubility which agreed with that of a specimen made by us from β-chlorlactic acid and also with that determined by Melikoff[1] for isoserin. Our acid is therefore the α-oxy-β-nitropropionic acid.

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[1] Emil Fischer and Leuchs : Ber. d. chem. Ges., 35, 3787 (1902).

EXPERIMENTAL PART.

The mucobromic acid used in this work was prepared by the method of Simonis,[2] that is, oxidizing furfurol with water and an excess of bromine. The mucobromic ethyl ester was made from this by warming the acid for several hours on the steam-bath with about three times its weight of alcohol containing 3 per cent of hydrochloric acid, after which the excess of alcohol was evaporated off and the residue poured into cold water. The brown crystalline mass thus obtained was purified by dissolving it in hot alcohol and bringing the solution to crystallization by plunging it in a freezing-mixture of ice and salt. The yield was 90 per cent of the weight of acid. The ester was also made by mixing equal weights of mucobromic acid and alcohol and strong sulphuric acid and allowing the mixture to stand in the cold.

Potassic Ethylnitromaleate, $C_2NO_2HCOOKCOOC_2H_5$.—Fifteen grams of the mucobromic ethyl ester were dissolved in 105 cc. of alcohol mixed with 42 cc. of water, and to this was added a solution of 22 grams of potassic nitrite also dissolved in a mixture of 105 cc. of alcohol with 42 cc. of water. The mixture was allowed to stand two or three days, during which time light-green crystals of the salt were gradually deposited, which were dried *in vacuo* and analyzed with the following results:

I. 0.5028 gram salt gave, on combustion, 0.5800 gram CO_2 and 0.1264 gram H_2O.

II. 0.7925 gram salt gave, on combustion, 0.9134 gram CO_2. The water was lost. In both these combustions the salt was mixed with chromic oxide.

III. 0.7358 gram salt gave 43.5 cc. moist N_2 at 20°.5 and 759.5 mm. pressure.

IV. 0.6381 gram salt gave 36.25 cc. moist N_2 at 19° and 775 mm. pressure.

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[1] Ber. d. chem. Ges., **13**, 1266.

[2] *Ibid.*, **32**, 2084 (1899).

V. 0.6417 gram salt gave 0.2445 gram K_2SO_4.

VI. 0.5091 gram salt gave 0.1943 gram K_2SO_4.

	Calculated for $KC_6H_6NO_6$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	31.71	31.45	31.44	....	....	....	....
H	2.64	2.81	....	....	....	....	....
N	6.17	....	....	6.47	6.37	....	....
K	17.22	....	....	....	....	17.10	17.14

The yield of potassic ethylnitromaleate was 60 per cent of the weight of mucobromic ester taken.

Properties of Potassic Ethylnitromaleate.—It crystallizes in colorless, clustered, flat prisms, which are sparingly soluble in cold water, more readily in hot water, and its solution, when boiled, develops an acid reaction. One part of it dissolves in 21.6 parts of water at 16°. It is somewhat soluble in boiling strong alcohol and can be recrystallized from dilute alcohol. It is a remarkably stable body, since evaporation to dryness with strong hydrochloric acid on the steam-bath produced no appreciable decomposition and all attempts to make salts with other metals from it by double decomposition failed, although the ammonium and aniline salts were obtained.

The aniline salt was prepared as follows: Ten grams of the potassium salt were treated with 200 cc. of water, 35 cc. of strong hydrochloric acid, and 5.8 grams of aniline dissolved in 15 cc. of hydrochloric acid and 10 cc. of water. The salt was purified by three recrystallizations from alcohol and analyzed with the following results:

I. 0.2278 gram salt gave, on combustion, 0.4249 gram CO_2 and 0.1086 gram H_2O.

II. 0.2572 gram salt gave 23.1 cc. moist N at 24° and 771 mm. pressure.

	Calculated for $C_2HNO_2COOC_2H_5COOHC_6H_5NH_2$.	Found.	
		I.	II.
C	51.07	50.87	....
H	4.96	5.30	....
N	9.93	....	10.24

Potassic Methylnitromaleate, $C_2NO_2HCOOKCOOCH_3$.—This substance was made by treating the mucobromic methyl ester with potassic nitrite in dilute alcohol in the way described under the ethyl compound.

I. 0.2470 gram substance gave, on evaporation with strong sulphuric acid, 0.1005 gram K_2SO_4.

II. 0.2505 gram substance gave 0.1023 gram K_2SO_4.

	Calculated for $C_2NO_2HCOOKCOOCH_3$.	Found. I.	II.
K	18.35	18.26	18.33

In its properties it resembles the ethyl compound most closely.

Action of Bromine and Water on Potassic Ethylnitromaleate.

Ten grams of the potassium salt were suspended in water and a stream of air saturated with bromine vapor passed through the mixture, until 2 molecules of bromine (14.08 grams) had been added for each molecule of the salt. During this operation a heavy oil with a penetrating odor separated from the liquid and collected in drops at the bottom of the vessel. After removing it from the water this was dried over calcic chloride and distilled twice, when it boiled from 158° to 163° with partial decomposition. Its analysis gave the following results:

I. 0.3493 gram oil gave, by the Carius method, 0.5874 gram AgBr.

II. 0.3363 gram oil gave 0.5638 gram AgBr.

	Calculated for $CHBr_2NO_2$.	Found. I.	II.
Br	73.07	71.56	71.35

The oil is therefore evidently dibromnitromethane. The yield was good, as 7.6 grams were obtained from 10 grams of the potassic ethylnitromaleate instead of 9.65 grams, that is, 78.8 per cent of the theoretical yield.

The solution from which the dibromnitromethane had been obtained was freed from it completely by neutralization with calcic carbonate and distilling with steam until no more of the oil passed over. The residue was then slightly acidified with hydrochloric acid and treated with a solution of the hydrochloride of phenylhydrazine; the precipitate thus obtained showed the melting-point 136° to 137°, which, although lower than 143° to 145°, that given by von Pechmann for the phenylhydrazone or glyoxylic acid, $C_6H_5NHNCHCOOH$, agrees well with the melting-points given by other observers. That it is this phenylhydrazone is proved by the following analyses :

I. 0.1945 gram substance gave, on combustion, 0.4162 gram CO_2 and 0.0923 gram H_2O.

II. 0.2220 gram substance gave 33.1 cc. N_2 at 24° and 765 mm. pressure.

III. 0.2499 gram substance gave 37.2 cc. N_2 at 23° and 758 mm. pressure.

	Calculated for $C_6H_5NHNCHCOOH$.	Found.		
		I.	II.	III.
C	58.54	58.34	....	....
H	4.88	5.33	....	....
N	17.08	....	16.83	16.72

Glyoxylic acid must therefore have been one of the products of the reaction of bromine on potassic ethylnitromaleate, which may be written as follows :

$$C_2NO_2HCOOKCOOC_2H_5 + 2Br_2 + 2H_2O = $$
$$CHBr_2NO_2 + C_2H_2O_3 + CO_2 + KBr + HBr + C_2H_5OH.$$

In order to prove that the glyoxylic acid was one of the products of the decomposition of the nitromaleic acid molecule and not formed by oxidation of the ethyl group the experiment was repeated with the potassic methylnitromaleate, and the glyoxylic acid found in this case also.

Action of Ammonia on the Potassic Ethylnitromaleate.

Nitromaleic Amide.—A portion of the potassium salt was dissolved in a solution of ammonic hydrate and allowed to stand at ordinary temperatures for some hours, when it was found that a heavy precipitate of yellowish-white needles had been thrown down, leaving but little organic matter in the solution. These crystals consisted of a mixture of the ammonium and potassium salts of the nitromaleamide,

$$C_2HNO_2CONH_2COOH.$$

Its composition was determined by the analyses of the silver and potassium salts prepared from it, as follows:

Silver Salt, $C_2HNO_2CONH_2COOAg$.—An aqueous solution of the mixed potassium and ammonium salts was treated with argentic nitrate, which threw down a nearly insoluble precipitate made up of minute white crystals; these were dried *in vacuo* and analyzed as follows:

0.3500 gram salt gave 0.2463 gram AgBr.

	Calculated for $C_2HNO_2CONH_2COOAg$.	Found.
Ag	40.45	40.41

Potassium Salt, $C_2HNO_2CONH_2COOK$.—A solution of the free amide was prepared by the cautious addition of hydrochloric acid to the silver salt. It was found that the amide was stable in solution at ordinary temperature, but was decomposed during evaporation to dryness. The potassium salt was made by treating the solution of the free amide with potassic carbonate. It was dried *in vacuo* and analyzed:

I. 0.2463 gram salt gave, on evaporation with sulphuric acid, 0.1061 gram K_2SO_4.

II. 0.2429 gram salt gave 0.1043 gram K_2SO_4.

	Calculated for $C_2HNO_2CONH_2COOK$.	Found.	
		I.	II.
K	19.73	19.35	19.27

The potassium salt forms white crystals very sparingly soluble in water whether hot or cold.

Ammonium Salt, $C_2HNO_2CONH_2COONH_4$.—This salt was made by allowing the aniline salt to stand for two or three days with a solution of ammonic hydrate. It gave the following results on analysis:

0.2517 gram substance gave, on combustion, 0.2528 gram CO_2 and 0.1002 gram H_2O.

	Calculated for $C_2HNO_2CONH_2COONH_4$.	Found.
C	27.11	27.39
H	3.95	4.42

It crystallizes in fine, white needles and is more soluble than the potassium salt.

Action of Baric Hydrate on Potassic Ethylnitromaleate.

Baric Nitromalate.—When a solution of potassic ethyl nitromaleate was treated with baric hydrate and enough baric chloride to replace the potassium, a new insoluble barium salt was formed which was evidently derived from another acid, since on the addition of hydrochloric acid carbonic dioxide was evolved and nitrolactic acid formed. The study of this salt offered great difficulties, because it could not be recrystallized owing to its insolubility, and the acid, as was just stated, decomposes as soon as set free. We could find no way, therefore, to purify it, and have analyses only of the salt as precipitated. These gave results varying from 52.17 to 53.40 per cent of barium in the air-dried salt and from 54.68 to 56.45 per cent in the salt dried at 100°. This variation indicates that the crude precipitate was contaminated with baric carbonate, which could hardly be avoided in a precipitate made with baric hydrate from a salt that decomposes with great ease into a carbonate and nitrolactate. The most probable formula for this barium salt, considering its relation to the nitromaleic acid on the one side and the nitrolactic on the other is $Ba_3(C_4H_2NO_7)_2$, a basic baric malate. The percentage of barium calculated for this formula is not far from those found.

	Calculated for $Ba_3(C_4H_2NO_7)_2$.	Found.
Ba	53.87	54.68–56.45

In view of its behavior with hydrochloric acid it was possible that this barium salt might be a mixture of nitrolactate formed directly from the nitromaleate and baric carbonate. This theory, however, was excluded by determining the amount of baric hydrate necessary to form the salt when baric hydrate alone was used. If it were the mixture of nitrolactate and carbonate, 2 molecules of baric hydrate would be necessary to each molecule of the potassic ethylnitromaleate, but in an actual experiment only 1.635 molecules were used in the complete formation of the salt, that is, the amount required to form the basic baric malate. This formula, therefore, can be adopted as the one which best represents the known facts.

β-Nitrolactic Acid, $CH_2NO_2CHOHCOOH$.—When the barium salt described in the preceding section was treated with dilute hydrochloric acid it dissolved with evolution of carbonic dioxide. The solution thus obtained was then treated with ether in a continuous extractor for three or four hours, and the extract, which consisted of a colorless mass of crystals, was purified by crystallization from ether and chloroform until it showed the constant melting-point 76° to 77°, when it was dried *in vacuo* and analyzed with the following results :

I. 0.2101 gram substance gave, on combustion, 0.2041 gram CO_2 and 0.0750 gram H_2O.

II. 0.1955 gram substance gave 0.1912 gram CO_2 and 0.0690 gram H_2O.

III. 0.1820 gram substance gave 16.8 cc. moist N_2 at 15°.5 and 766 mm. pressure.

	Calculated for $CH_2NO_2CHOHCOOH$.	Found. I.	II.	III.
C	26.67	26.50	26.67	....
H	3.70	3.96	3.92	....
N	10.37	....	....	10.82

Properties of β-Nitrolactic Acid.—It crystallizes from ether and chloroform in small, irregular, white prisms, which melt at 76° to 77° (uncorr.). It is very soluble in water, alcohol, or ether ; more sparingly soluble in chloroform. As this nitrolactic acid contains an unsymmetrical carbon atom, a preliminary attempt was made to resolve it into its optically active isomers. Seven grams of the acid were converted into its strychnine salt, which was then recrystallized from hot water until two successive filtrates gave a constant angle, when tested in the polariscope. The salt thus obtained was dissolved in water, acidified with hydrochloric acid, and the active nitrolactic acid extracted with ether. 0.3494 gram of this acid gave a laevo rotation of 0°.69, which corresponds to a specific rotation of about 20°.

Argentic Nitrolactate, $CH_2NO_2CHOHCOOAg$.—An aqueous solution of nitrolactic acid was warmed gently with an excess of argentic carbonate and filtered hot, when, on cooling, the silver salt crystallized from the filtrate. It was dried *in vacuo* and analyzed with the following result:

0.1808 gram salt gave 0.1410 gram AgBr.

	Calculated for $CH_2NO_2CHOHCOOAg$.	Found.
Ag	44.63	44.79

The salt crystallizes from warm water in fine, white needles, which are decomposed by direct sunlight. It is stable in aqueous or acid solutions, but decomposes in presence of alkalies.

Barium Salts of Nitrolactic Acid.—When nitrolactic acid was warmed in aqueous solution with baric carbonate the product was an unmanageable amorphous wax. If, however, an aqueous solution of the acid was treated with baric hydrate, a slightly pinkish precipitate was obtained which gave the following results on analysis:

I. 0.2240 gram substance gave, on evaporation with sulphuric acid, 0.2007 gram $BaSO_4$.

II. 0.2493 gram substance gave 0.2233 gram $BaSO_4$.

III. 0.2414 gram substance gave 0.2160 gram $BaSO_4$.

	Calculated for $(CH_2NO_2CHOCOO)Ba$.	Found.		
		I.	II.	III.
Ba	50.74	52.67	52.66	52.61

The percentages of barium found are decidedly too high, but in a precipitate made with baric hydrate enough baric carbonate might be present to raise the percentages found 2 per cent. Upon acidification the barium salt gives nitrolactic acid, which seems to exclude the formation of an anhydride, or any similar reaction which would give theoretical numbers agreeing more nearly with those found.

Calcic carbonate gave a white crystalline salt when warmed with an aqueous solution of nitrolactic acid.

Acetnitrolactic Acid, $CH_2NO_2CHOC_2H_3OCOOH$.—This substance was prepared by heating nitrolactic acid on the steam-bath for two or three hours with an excess of acetic anhydride. The unaltered acetic anhydride was then evaporated off and the crystalline residue purified by recrystallization from ether and chloroform until it showed the constant melting-point 90° to 91°, when it was dried *in vacuo* and analyzed with the following result:

I. 0.1797 gram substance gave, on combustion, 0.2250 gram CO_2 and 0.0646 gram H_2O.

II. 0.1547 gram substance gave 11.2 cc. moist N_2 at 20°.5 and 768 mm. pressure.

	Calculated for $CH_2NO_2CHOC_2H_3OCOOH$.	Found.	
		I.	II.
C	33.90	34.14	....
H	3.95	3.99	....
N	7.93	....	8.12

The acetnitrolactic acid crystallizes from a mixture of ether and chloroform in large, perfect, white octahedra, freely soluble in water.

Argentic Acetnitrolactate, $CH_2NO_2CHOC_2H_3OCOOAg$.—This salt was obtained by mixing strong aqueous solutions of the acetnitrolactic acid and argentic nitrate, the crystals which separated were washed with water, dried *in vacuo*, and analyzed with the following result:

0.2165 gram substance gave 0.1082 gram AgCl.

	Calculated for $CH_2NO_2CHOC_2H_3OCOOAg$.	Found:
Ag	38.03	37.61

It crystallizes in bunches of gleaming white needles and is decomposed by heating with water, which is strange, as the argentic nitrolactate is stable under these conditions.

The Reduction of Nitrolactic Acid.

Isoserin, $CH_2NH_2CHOHCOOH$.—The nitrolactic acid was heated with tin and strong hydrochloric acid diluted with its own volume of water in a small flask on the steam-bath for two or three hours. The tin was then precipitated by sulphuretted hydrogen and the chloride of the amido compound in the filtrate decomposed with argentic oxide. Finally the silver, which had dissolved, was removed with sulphuretted hydrogen. On concentrating the final filtrate the product was deposited in small, hard crystals, which, dried *in vacuo*, gave the following results on analysis :

I. 0.2098 gram substance gave, on combustion, 0.2612 gram CO_2 and 0.1244 gram H_2O.

II. 0.1835 gram substance gave 21.7 cc. moist N_2 at 17° and 742 mm. pressure.

	Calculated for $CH_2NH_2CHOHCOOH$.	Found. I.	Found. II.
C	34.29	33.95	....
H	6.67	6.59	....
N	13.32	....	13.42

These results showed that the substance was an amidolactic acid, but it remained to be determined whether it was serin, α-amido-β-oxypropionic acid, or isoserin, α-oxy-β-amidopropionic acid. The crystalline form—small, hard, nearly cubic crystals—did not agree with the long, thin, monoclinic prisms, the form assigned to isoserin by Haushofer,[1] and, accordingly, to settle the question we made the copper salt, which Emil Fischer and Leuchs[2] have shown is very characteristic, and also determined the solubility of the free acid.

The copper salt, dried at 100°, gave the following results on analysis :

I. 0.2525 gram salt gave 0.1184 gram cupric oxide.

II. 0.1884 gram salt gave 0.0893 gram cupric oxide.

	Calculated for $C_3H_5O_3NCu$.	Found. I.	Found. II.
Cu	38.10	37.44	37.85

These low results are explained by the observation of Emil Fischer that the copper salt of isoserin retains water even when dried at 110°. Unfortunately, his paper did not reach us until this part of the work was finished, so that we cannot give analyses of thoroughly dried specimens. This, however, is not necessary, as these results prove that the formula is $CuC_3H_5O_3N$, characteristic of the isoserin, and not the salt $Cu(C_3H_6O_3N)_2$ of the serin.

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[1] Jsb., 1880, p. 779.

[2] Ber. d. chem. Ges., **35**, 3787 (1902).

To settle the identity of our substance beyond question we compared its solubility with that of some isoserin made from β-chlorlactic acid, and purified by several recrystallizations, conversion into the copper salt, decomposition with sulphuretted hydrogen, and finally crystallization from hot water. The specimen of isoserin from the nitrolactic acid was purified by careful recrystallization.

I. 7.1943 grams of a solution of isoserin from nitrolactic acid, saturated at 20°, contained 0.1087 gram solid.

II. 8.2879 grams of a solution of isoserin from β-chlorlactic acid, saturated at 20°, contained 0.1251 gram solid.

Parts of water necessary to dissolve one part of isoserin.

I.	II.
65.16	65.27

These results agree with those of Melikoff,[1] who found that 1 part of isoserin dissolves in 65.4 parts of water, whereas 1 part of serin[2] dissolves in 24.7 parts of water. There can be no doubt, therefore, that our substance is isoserin.

A METHOD FOR THE DETERMINATION OF CHLORIC ACID.

By W. S. Hendrixson.

In the methods for the determination of chloric acid by reduction, metallic zinc, in some form, and ferrous sulphate have been the reducing agents most used, though several others, including sulphur dioxide and formic aldehyde, have been employed. The conditions under which zinc and ferrous sulphate have been used have been much varied. Thorpe[3] and Thorpe and Eccles[4] used the zinc-copper couple to reduce chlorates and determined the chloride, resulting from the chlorate, with a solution of silver. Bothamley and Thompson[5] showed that the results by this method were too low unless sulphuric acid was added near the end of the reduction to dissolve any basic salts of zinc. By the same method Becker[1] also found the results too low and preferred to use zinc dust and a little copper sulphate. Fleissner[2] used zinc dust and boiled the solution one hour, but Becker attained complete reduction only by using a large excess of zinc dust with sufficient sulphuric acid to dissolve it completely without the aid of heat.

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[1] Ber. d. chem. Ges., **13**, 1266 (1880).

[2] Erlenmeyer, *Ibid.*, **13**, 1078 (1880); Cramer: J. prakt. Chem., **96**, 94 (1865).

[3] J. Chem. Soc. (London), **11**, 541.

[4] *Ibid.*, **14**, 856.

[5] *Ibid.*, **53**, 164.

Stelling[3] reduced chlorates by long boiling with ferrous sulphate, in alkaline solution, and determined the resulting chloride. Becker found that the reaction was very slow and incomplete, and recommended a neutral solution of ferrous sulphate. Carno[4] reduced the chlorates in bleaching-powder by heating at 100° with a large excess of ammonium ferrous sulphate and an excess of sulphuric acid. The amount of chlorate was found either by titrating the resulting chloride by the method of Volhard or by determining the excess of ferrous sulphate with permanganate. Rosenbaum[5] states that chlorine will be lost in this method of reduction if the acid and the ferrous sulphate are added to a hot solution of the chlorate.

In the course of my work on the action of chloric acid on metals,[6] it was observed that metallic iron very readily reduces free chloric acid even in very dilute solutions. At ordinary room temperature the solution of the metal is very rapid in moderately concentrated solutions of the acid, and the iron goes at once into the ferric condition, as was proved by many tests while solution was going on. No gas is evolved, but the iron simply disappears and there results the yellowish-brown solution of ferric salt, and the solution remains clear if the acid is in considerable excess. Whether iron alone thus reduces chloric acid completely could not be determined with accuracy, owing to the fact that toward the end of the reaction large amounts of oxide and possibly basic salt are necessarily formed, and these make it impracticable to obtain a solution suitable for titration with silver without the use of agents which would also decompose chloric acid. An approximation, however, showed that at least 95 per cent of the chloric acid was reduced. These facts suggested that the determination of chloric acid might be brought to a very simple form by using metallic iron as the chief reducing agent in the presence of an excess of sulphuric acid, which would prevent the formation of insoluble compounds, make the method applicable to chlorates by setting free the chloric acid, and form ferrous sulphate, which is itself a reducing agent for chloric acid, and which would already be present to serve, when oxidized, as the indicator in the titration of the chloride formed, by the method of Volhard. It is evident, therefore, that such a method would be a very simple combination of the two general methods already mentioned, the reduction of chloric acid by a metal, and probably a more efficient one than zinc, and the reduction by ferrous sulphate.

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[1] Repert. anal. Chem., **1**, 377.
[2] Ztschr. anal. Chem., **30**, 115.
[3] *Ibid.*, **6**, 32.
[4] Compt. rend., **122**, 449.
[5] Ztschr. angew. Chem., 1893, 80.
[6] J. Am. Chem. Soc., **26**, 747.

To carry out the method a weighed amount of pure potassium chlorate or a measured volume of chloric acid of known strength was placed in a small flask with about 50 cc. of pure sulphuric acid having a concentration of about 10 per cent, and an excess of "card-teeth" used in most laboratories as a convenient form of iron. In some of the experiments recorded below, the flask was fitted with a delivery-tube which dipped into water, the purpose being to prevent the possible loss of hydrochloric acid, a precaution which at room temperature was proved to be wholly unnecessary. At first ferric salt is formed and gives the solution the characteristic color due to ferric salts, but the salt is soon reduced and the solution becomes colorless or slightly green. If all the chlorate is dissolved at the beginning of the experiment, the disappearance of the yellow color may be taken to mark the end of the reduction, which requires, at room temperature, about one hour. No doubt the reduction could be hastened by heating, if precaution were taken to prevent the loss of hydrochloric acid by volatilization. As might naturally be expected, the method serves quite as well for bromic acid and bromates as for chloric acid and chlorates, and two determinations of the bromic acid in potassium bromate are given below.

After the reduction was completed the solution was made up to a definite volume and portions of it were titrated with N/20 silver nitrate by Volhard's method. Usually an excess of silver was added before the iron was oxidized with an excess of nitric acid to the ferric condition to serve as the indicator. There seems, however, to be little danger of the loss of chlorine if the nitric acid is added before the silver.

The following are results obtained by the method described, the amounts of silver required in the titrations being calculated to chloric acid or bromic acid:

1. 5 cc. of a solution of chloric acid gave 1.0639 grams $HClO_3$.

2. 5 cc. of the same solution gave 1.0619 grams $HClO_3$.

The same solution, titrated with standard barium hydroxide gave, in 5 cc., 1.0665 grams $HClO_3$.

3. 0.4595 gram $KClO_3$ gave 0.3158 gram $HClO_3$; calculated, 0.3165 gram.

4. 0.6709 gram $KClO_3$ gave 0.4628 gram $HClO_3$; calculated, 0.4622 gram.

5. 0.8300 gram $KClO_3$ gave 0.5731 gram $HClO_3$; calculated, 0.5718 gram.

6. 1.2744 grams $KClO_3$ gave 0.8778 gram $HClO_3$; calculated, 0.8778 gram.

7. 0.3350 gram $KBrO_3$ gave 0.2605 gram $HBrO_3$; calculated, 0.2585 gram.

8. 1.0983 grams $KBrO_3$ gave 0.8460 gram $HBrO_3$; calculated, 0.8478 gram.

The method above described seems to have some advantages. It is extremely simple. It can be carried out at room temperature, avoiding any danger of the loss of hydrochloric acid by heating. In the reduction and the preparation of the solution for titration are necessary only iron and pure sulphuric and nitric acids, which are always at hand in every laboratory, and no filtering or other operations likely to occasion loss of chlorine or loss of time are required.

Perchloric acid shows the same indifference toward metallic iron as toward most other reducing agents, and does not, therefore, interfere in the determination of chloric acid by this method.

IOWA COLLEGE, GRINNELL, IA.,
March 18, 1904.

Contributions from the Sheffield Laboratory of Yale University.

ON THE SOLUBILITY OF BARIUM AND MERCURIC CHLORIDES.

BY H. W. FOOTE AND H. S. BRISTOL.

A double salt of mercuric and barium chlorides has been described by Bonsdorf,[1] who assigned the formula

$$BaCl_2.2HgCl_2.2H_2O.$$

As double salts containing barium chloride are almost unknown, we decided to test for its existence in crystal form by means of the solubility method which has previously been described.[2] The experiments were carried out first at 25°. Mixtures of barium chloride and mercuric chloride were prepared in varying proportions and treated with enough water to dissolve them when hot, allowing a crystal mass to form on cooling containing both mercuric and barium chlorides. In case no double salt formed, the solubility of the mixtures would be the same in all experiments while the composition of the residue which crystallized could vary between pure barium chloride on the one hand and pure mercuric chloride on the other. The solubility of the mixtures would not be the same throughout the series in case a double salt formed.

The mixtures, after being prepared as above described, were rotated in a thermostat for several days, when a sample of the solution was drawn off in a pipette through a filter of glass wool and analyzed. The residues were then removed, dried as quickly as possible between filter-paper, and analyzed. The analysis of both solution and residue was carried out by precipitating the solution, containing hydrochloric acid, with hydrogen sulphide. Mercuric sulphide was filtered off on a Gooch crucible, dried at 100° to 120°, and weighed. Barium was determined in the filtrate as sulphate. Water was calculated by difference. The following percentages were obtained at 25°:

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[1] Pogg. Ann., **17**, 130 (1829).

[2] This JOURNAL, **30**, 330, 339 (1903).

Table I.—Solubility of Mixtures of Barium and Mercuric Chlorides at 25°.

	$BaCl_2$ in solution.	$HgCl_2$ in solution.	$BaCl_2$ in residue.	$HgCl_2$ in residue.	H_2O in residue.
1	23.09	54.66	83.40	2.77	13.83
2	23.07	54.91	39.34	54.22	6.44
3	22.69	55.00	17.72	79.35	2.93
4	23.26	54.75	12.87	84.97	2.16
5	23.00	54.85	4.84	94.49	0.67

It will be noticed that the composition of the solutions remains practically constant throughout the series, while the residues vary between extreme limits, showing that *no double salt crystallizes at 25°*.

The solubility of each salt in water is largely increased by the presence of the other, indicating the formation of a complex salt in solution. It was therefore thought possible that a double salt might form at another temperature. Bonsdorf mentions that he obtained his double salt in the cold. To determine whether a double salt formed at some other temperature, a dilatometer was filled with a mixture of barium and mercuric chlorides moistened with the saturated solution of the salts, and with toluene to fill the air spaces and register the change in volume. A decided change in volume was observed between 17° and 18°, indicating a change in the solid phase. This was afterwards shown to be due to a double salt.

The dilatometer readings with the corresponding temperatures are given in Table II.

The dilatometer was cooled and warmed alternately to allow a mixture of the double salts and single salts to form. Placed again in a bath at 17°.6 the column gradually rose from 14.3 mm. to 14.9 mm. At 17° the column fell from 11.4 to 8.2 mm. The transition temperature would therefore be about 17°.2. The results in Table II. are shown graphically in Fig. I. The temperature is plotted as abscissa and the dilatometer readings as ordinate.

Table II.

Temperature.	Height of toluene in mm.
—3°.4	0.8
—1°.4	1.2
+1°.6	1.95
2°.6	2.45
5°.6	3.6
14°.6	6.1
16°.5	6.8
16°.7	6.9
17°.4	7.9
17°.6	11.8
18°.6	14.4
25°.6	18.3

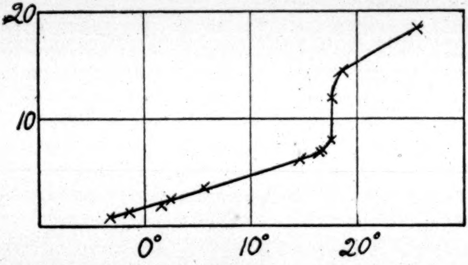

Fig. I.

To determine what change takes place at and below 17°.2, as indicated by the dilatometer, the solubility of mixtures of the two salts was determined at 10°.4. A constant temperature was obtained by means of the low-temperature thermostat described by one of us.[1] As the double salt which forms at this temperature was but a few degrees below its transition temperature where it breaks down into mercuric chloride and barium chloride, it was to be expected that the limits of its solubility would be very narrow, and this was found to be the case. It was prepared pure only after some trouble though mixtures of it with barium chloride or mercuric chloride were readily obtained. If solutions were prepared which were much supersaturated at 10°, only mixtures could be obtained of the double salt with one of the single salts, due to the fact that the single salts are not present in the same proportion in both solution and solid. On the other hand, if solutions were prepared which were but slightly supersaturated no salt would crystallize on shaking. The method adopted to obtain the pure double salt was to prepare solutions slightly supersaturated at the temperature of the experiment. To these solutions a minute quantity of crystals of the double salt and a single salt was added to start the crystallization. These crystals were obtained from a solution which was so much supersaturated that it would crystallize of itself. In this way pure double salt could be obtained which was proved by the fact that the composition of the solutions yielding the double salt varied somewhat while the composition of the residue remained practically constant.

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[1] Ztschr. phys. Chem., 33, 749 (1900).

The solubility results at 10°.4 are in Table III. In criticizing them, it must be remembered that the composition of the solution could be determined much more accurately than that of the residue, as the latter was contaminated with a certain amount of the mother-liquor containing a large proportion of dissolved salts.

In Nos 8 to 11 of the above table the pure double salt was present, as the solution varied, while the residue was nearly constant. The results on the composition of the residue are italicized in this case. They correspond closely to the salt $BaCl_2.3HgCl_2.6H_2O$, the calculated composition of which is added in the table.

That the salt decomposes at the temperature of a warm room was shown qualitatively by samples of the salt, which partly liquefied in tightly closed specimen-tubes. A salt with the formula given by Bonsdorf, $BaCl_2.2HgCl_2.2H_2O$, could not liquefy, as on decomposing the water, would be present in the right proportion to form crystallized barium chloride.

Table III.—Solubility of Mixtures of Barium and Mercuric Chlorides at 10°.4.

	$BaCl_2$ in solution. Per cent.	$HgCl_2$ in solution. Per cent.	$BaCl_2$ in residue. Per cent.	$HgCl_2$ in residue. Per cent.	H_2O in residue. Per cent.
1	23.55	50.54	66.94	21.27	11.79
2	23.48	50.59	49.25	38.00	12.75
3	23.69	50.55	28.80	59.55	11.65
4	23.62	50.41	22.50	66.47	11.03
5	23.52	50.65	21.41	67.50	11.09
6	23.57	50.56	19.56	69.90	10.54
7	23.64	50.51	19.36	70.06	10.58
8	23.44	50.74	*18.75*	*70.80*	*10.45*
9	22.58	51.23	*18.82*	*72.08*	*9.10*
10	22.48	51.41	*18.96*	*70.71*	*10.33*
11	22.10	51.66	*18.88*	*71.87*	*9.25*
(Calculated for $BaCl_2.3HgCl_2.6H_2O$)			18.45	71.98	9.57
12	21.69	52.01	15.13	79.87	5.00
13	21.55	51.69	3.21	95.55	1.24
14	21.68	52.11	0.78	99.27	....

The solubility results at 25° and 10°.4 are shown in Fig. II.

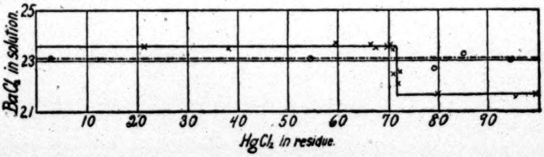

Fig. II.

The percentage of mercuric chloride in the residue is plotted as abscissa and the percentage of barium chloride in the solution as ordinate. The dotted horizontal line represents the solubility at 25°, where no double salt formed, and the other the solubilities at 10°.4.

Summary.

In the preceding article it has been shown :

1. That barium and mercuric chlorides do not form a double salt at 25°.

2. That a transition temperature exists at about 17°.2, below which the salt $BaCl_2.3HgCl_2.6H_2O$ forms.

3. That the salt $BaCl_2.2HgCl_2.2H_2O$, described by Bonsdorf does not form under the conditions which he gives. The solubility method, previously described, has been used to detect the presence of the double salt.

NEW HAVEN, CONN., March, 1904.

Contributions from the Sheffield Laboratory of Yale University.

ON THE SOLUBILITY OF POTASSIUM AND BARIUM NITRATES AND CHLORIDES.

BY H. W. FOOTE.

The double nitrate of potassium and barium,

$$2KNO_3.Ba(NO_3)_2,$$

was described recently by Wallbridge.[1] As this salt was very unexpected, its solubility relations have been determined at 25° by the solubility method previously given. The solutions obtained were analyzed by evaporating them to dryness and weighing the residue after very gentle ignition. The residue was dissolved in water and barium determined as sulphate, after which potassium nitrate could be calculated. The composition of the residue was usually calculated, as water was absent. This could be done with sufficient accuracy by starting with known amounts of the two single salts and water. In one or two cases barium was determined as a check on this value.

The results obtained are in Table I., columns II. and III., showing the parts of potassium nitrate and barium nitrate, respectively, in 100 parts of solution. Where the pure double salt is present, the composition of the residue remains practically constant, while the solution varies. These results are italicized. In the other results, where a mixture was present either of potassium nitrate and the double salt (Nos. 6 to 9) or of the double salt and barium nitrate (Nos. 1 to 3) the composition of the residue varies while the solubility remains constant.

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[1] This JOURNAL, 30, 154 (1903).

Table I.—Solubility of Potassium and Barium Nitrates at 25°.

I.	II. KNO_3 in solution.	III. $Ba(NO_3)_2$ in solution.	IV. KNO_3 in residue.	V. Residue contains :
1	15.24	6.64	5.14	$Ba(NO_3)_2$ and $2KNO_3.Ba(NO_3)_2$
2	14.69	6.60	26.76	" " "
3	14.79	6.62	38.66	" " "
4	*16.30*	*5.49*	*43.45*	$2KNO_3.Ba(NO_3)_2$
5	*21.99*	*3.04*	*43.25*	"
				(Calculated percentage of KNO_3 = 43.65)
6	27.66	2.01	50.52	KNO_3 and $2KNO_3.Ba(NO_3)_2$
7	27.81	2.09	64.10	" " "
8	27.94	1.92	81.27	" " "
9	27.64	2.05	93.45	" " "

The results in the table are represented graphically in Fig. I. The percentages of potassium nitrate in solution and in the residue are plotted respectively as ordinate and abscissa.

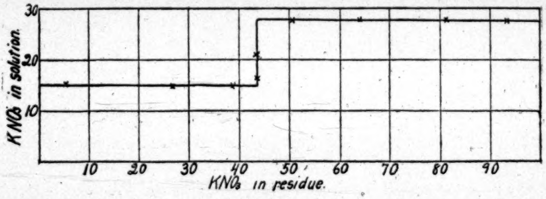

Fig. I.

The results show that the double salt can form at 25° under a moderately wide range of conditions, that is, it can form from solutions containing approximately from 15 to 27 per cent of potassium nitrate and from 6 to 2 per cent of barium nitrate.

The salt cannot be recrystallized, but would deposit at first crystals of barium nitrate if evaporated at 25°. This is shown by the fact that the solution of the double salt would contain a greater percentage of barium nitrate than of potassium nitrate, while all the solutions obtained above, including those in equilibrium with barium nitrate and the double salt, contain an excess of potassium nitrate.

A double salt of potassium and barium chlorides has never been prepared, and the solubility results given below in Table II. show that none forms at 25°.

Table II.—Solubility of Potassium and Barium Chlorides at 25°.

	KCl in solution. Per cent.	$BaCl_2$ in solution. Per cent.	KCl in residue. Per cent.
1	18.97	13.86	9.64
2	18.96	13.85	98.37

Had a double salt formed the solubility in the first experiment where a large excess of barium chloride was present would be different from the solubility in the second experiment, where the residue was nearly pure potassium chloride.

From results obtained by Rüdorf[1] on the solubility of mixtures of salts, it is very probable that ammonium chloride and sodium chloride also form no double salts with barium chloride.

New Haven, Conn., March, 1904.

ON SOME CUPRAMMONIUM SULPHATES.

By David W. Horn and Edytha E. Taylor.

The extensive investigations recently carried out on solutions of cuprammonium salts have made it desirable that the salts themselves be isolated and studied. This paper deals mostly with the cuprammonium sulphate longest known among the metal-ammonium compounds,

$$CuSO_4 + 4NH_3 + H_2O,$$

and the decomposition-products that have been given the formulas

$$CuSO_4 + 2NH_3 \quad \text{and} \quad CuSO_4 + NH_3.$$

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[1] Pogg. Ann., 148, 467; Berliner Akad. Ber., 1885, 355.

Of these formulas, $CuSO_4 + 4NH_3 + H_2O$ has rested upon one analysis made by Berzelius[1] of apparently the same salt to which Bouzat has but recently[2] assigned a different formula—

$$CuSO_4 + 4NH_3 + 3/2H_2O.$$

The formulas $CuSO_4 + 2NH_3$ and $CuSO_4 + NH_3$ have had no basis in fact except the losses in weight observed by Kane[3] when the salt stated by Berzelius to be

$$CuSO_4 + 4NH_3 + H_2O$$

is heated at different temperatures. Changes in weight cannot be relied upon to differentiate ammonia having a molecular weight of 17 from water having a molecular weight of 18, even when the original substance is known to have a definite composition. For these reasons we proposed to prepare these substances, insuring the reliability of our preparations by complete analyses. Such analyses involve the difficulty of determining ammonia and water in a mixture of the vapors of the two, as well as that of determining sulphuric acid in copper compounds. We worked out reliable analytical methods and then studied the preparation and properties of the salt

$$CuSO_4 + 4NH_3 + H_2O,$$

its behavior at elevated temperatures, and the properties of its aqueous solution. This paper presents these points in order.

I. Analytical Methods.

(*A*) *Determination of Copper.*—We first tried a rapid electrolytic method proposed by Wagner[4] for the determination of copper. The deposits were not uniform, but contained here and there brownish lumps. When the electrolysis was pushed so far that hydrogen sulphide no longer gave a precipitate in the liquid that was being electrolyzed, the results were high. This is illustrated by the following analysis:

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[1] Gilbert's Ann., **40**, 300.

[2] Ann. chim. phys., [7], **29**, 305 (1903).

[3] *Ibid.*, [2], **72**, 265.

[4] Ztschr. Elektrotech. u. Elektrochem., **2**, 613–616.

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
1.0081	0.2621	25.99	25.86

We then adopted Rose's method[1] of heating the dehydrated sulphates with sulphur in an atmosphere of hydrogen. The following analyses are given to show the degree of accuracy of the method:

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.5419	0.1401	25.87	25.86
0.4059	0.1049	25.87	
0.7004	0.1812	25.87	
0.5650	0.1463	25.89	
0.3632	0.0939	25.86	
0.5382	0.1392	25.87	
0.2811	0.0726	25.83	
0.4356	0.1126	25.86	
0.3921	0.1014	25.89	
0.4914	0.1271	25.84	
0.3146	0.0813	25.84	
0.3710	0.0960	25.87	

(*B*) *Determination of Ammonia.*—The usual method of distillation with an alkali was used. When the alkali was previously treated with potassium permanganate the results were invariably low in the case of copper compounds, although when ammonium borate was used to test the method the results were good. We used sodium hydroxide free from nitrogen. Lime was added to the alkaline liquids to prevent "bumping" during the distillations. It was found that the ammonia could only be completely removed from the copper compounds when the distillations were continued until the residues in the distilling-flasks reached approximately the concentration of 1 gram sodium hydroxide in 1 cc. to 1.5 cc. of the liquid. In order to prevent the mechanical carrying-over of alkali in the distillations we found it advisable to use long-necked balloon-flasks of about 2.5 liters capacity, and to distil at such a rate that the condenser-tube was but

[1] Anal. Chem., II., 173-4 (sixth German edition.)

one-fourth to one-third full of uncondensed water-vapor. To avoid loss of ammonia the salts were weighed into a slight excess of acid contained in the distilling-flasks. The following analyses of the salt $CuSO_4 + 4NH_3 + H_2O$ show to what extent the method can be relied upon when the precautions mentioned are taken :

Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.3521	0.0980	27.82	27.76
0.3969	0.1099	27.70	
0.2974	0.0825	27.76	
0.5006	0.1393	27.82	
0.3806	0.1057	27.77	
0.3049	0.0844	27.71	
0.4766	0.1322	27.74	

As already mentioned, ammonium borate may be used advantageously in testing the apparatus in the distillations, because the ammonia in it can be determined by direct titration as well as by distillation.

(*C*) *Determination of Water and Ammonia.*—Water and ammonia are evolved simultaneously by the salt $CuSO_4 + 4NH_3 + H_2O$ when it is heated. We determined them by heating a weighed quantity of the salt in a boat in a tube so arranged that a current of air, dry and free from carbon dioxide, could pass over the heated material and carry the water and ammonia evolved into absorption apparatus. We used air that had been passed through dilute sulphuric acid and barium hydroxide solutions, and then over solid sodium hydroxide and potassium hydroxide. The air leaving this apparatus entered the tube containing the boat through a piece of ordinary glass tubing about 2 meters long. The end of this connecting tube nearest the boat was drawn to a capillary tip in order to prevent as far as possible the diffusion of the ammonia backward toward the apparatus for purifying the air. The larger tube, in which the boat was heated, was placed in a cylindrical air-bath of about four times the length of the boat. This tube was joined directly to the absorption-apparatus consisting of two glass-stoppered U-tubes filled with solid potassium hydroxide to absorb the water evolved, and a similar tube containing glass beads and 65 per cent sulphuric acid (to absorb the ammonia) joined with two more tubes of potassium hydroxide to absorb the water given off by the acid. We tested this apparatus and method for the determination of water using crystallized barium chloride, the loss in weight of the boat checking on the changes in weight in the absorption-tubes. There was no occasion to test the absorption of ammonia by the acid. The results of eight analyses made by this method are given below, on pages 272 and 273.

The current of air used in these and other similar experiments was furnished by a simple apparatus that has since been found so useful in the laboratory that it will be described. A Bunsen pump passing through a rubber stopper is fitted into the middle opening of a Wolff bottle; into one of the side openings a siphon-tube is fitted by a rubber stopper, the arm of the tube within the bottle reaching almost to the bottom of the bottle; into the other opening there is fitted a tube bent at a right angle and cut off just beneath the rubber stopper through which it passes. The pump supplies water and air, the former being drawn off or forced out through the siphon-tube and the latter being drawn as needed from the other (outlet) tube. In using this apparatus the only precaution to be observed is that neither water nor air be drawn off faster than it is supplied by the pump. If the outlet of the siphon-tube be small, the air is supplied under considerable pressure.

(*D*) *Determination of Sulphuric Acid.*—Precipitated barium sulphate "carries down" copper salts[1] perhaps more freely than it does iron salts. For this reason it is imperative that the copper and sulphuric acid be separated quantitatively, leaving the latter under such conditions that it can be precipitated as (relatively) pure barium sulphate.

It is apparent that in this case the copper cannot be precipitated as sulphide. Gibbs proposed[2] to precipitate copper with sodium carbonate. We precipitated copper by this method as directed in Fresenius' "Quantitative Analysis,"[1] after we had treated the salt with a slight excess of dilute hydrochloric acid. The following were the results obtained by the careful precipitation of barium sulphate in the filtrates from the copper precipitates after an excess of hydrochloric acid had been added to these filtrates :

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[1] Berzelius: Ann. chim. phys., [2], 14, 376.

[2] Ztschr. anal. Chem., 7, 258.

Weight of salt taken for analysis. Gram.	Weight of SO_4 found. Gram.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.2832	0.0825	29.12	39.06
0.3666	0.1076	29.36	
0.2522	0.0763	30.25	
0.3754	0.1108	29.52	

These figures showed that the precipitates contained sulphuric acid which had been retained although the precipitates had been washed till the wash-waters no longer reacted with barium chloride. The presence of sulphuric acid in similar precipitates was proven later by qualitative tests, which also showed that the precipitates consisted partly of carbonates. The four original precipitates were analyzed for copper by Rose's method. The results showed the completeness of the previous precipitations of copper, and that the precipitates could be washed free from alkali salts ; they also served along with the sulphuric acid determinations already given to show that the proportion of copper to sulphuric acid in the (Gibbs) precipitates is very approximately 4 : 1.

Number of precipitate taken.	Weight of copper found. Gram.	Percentage of copper found in salt.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
1	0.0733	25.87	25.86
2	0.0952	25.97	
3	0.0654	25.93	
4	0.0971	25.87	

The advantages of Gibbs' method for precipitating copper are sufficiently clear. However, it cannot be used to separate sulphuric acid from copper because the green precipitate contains one equivalent of sulphuric acid to every four of copper present.

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[1] Sixth German edition, I., 331.

The copper was next precipitated as hydroxide by the addition of caustic potash to solutions of the salt (previously made slightly acid with hydrochloric acid), according to the directions of Fresenius.[1] The precipitates were difficult to wash and when tested qualitatively were always found to contain sulphuric acid, although the wash-waters from them had no longer reacted with barium chloride. The following analyses (1–4) of the precipitates for copper by Rose's method show that they had probably retained alkali salts in addition to the sulphuric acid already mentioned; analyses 5 and 6 were made by applying Rose's method to the original salt and are given for comparison:

Number of analysis.	Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
1	0.3474	0.0913	26.23	25.86
2	0.4444	0.1168	26.28	
3	0.6471	0.1690	26.11	
4	0.5107	0.1337	26.17	
5	0.3146	0.0813	25.84	
6	0.3546	0.0916	25.85	

We next tried adding the solution of the copper salt, previously acidified with hydrochloric acid, to an excess of caustic soda. The precipitates thus formed are comparatively easily washed, and afterward do not contain any sulphuric acid. Further, in this procedure it is not necessary to use a large excess of alkali so that after the filtrates have been acidified and before the sulphuric acid in them is precipitated they contain comparatively small amounts of alkali salts. This is an advantage, because alkali salts are also "carried down" by barium sulphate. There is a further advantage in using caustic soda, for potassium salts are "carried down" in larger quantities than sodium salts.[2] The results given on page 267 show the degree of accuracy of this method. In detail, the procedure was as follows:

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[1] *Loc. cit.*, p. 329.

[2] Kretschy: Ztschr. anal. Chem., **10**, 396.

A quantity of the copper salt containing about 0.09 gram of copper was weighed into a small beaker containing about 50 cc. of water. Hydrochloric acid was then added until the precipitate at first formed had completely redissolved. About 150 cc. of a solution of sodium hydroxide (free from sulphates), containing 2 grams of sodium hydroxide per liter, were heated to boiling in a large beaker. The copper solution was slowly stirred into the boiling liquid, the transfer being completed with water. The mixture was boiled gently for a few minutes and then digested for about half an hour just below the boiling temperature. The solution was filtered while hot. The precipitate, which had been retained in the beaker, was washed four times by decantation with hot water; it was then transferred to the filter and again washed with hot water until the wash-waters did not give a precipitate with barium chloride. The precipitate was then tested for sulphuric acid after it had been dissolved in dilute hydrochloric acid. The entire filtrate was acidified with hydrochloric acid and treated with an excess of barium chloride, observing the well-known precautions. The barium sulphate was treated as is usual.

The suggestion of Küster and Thiel to "remove the ion"[1] that interferes in precipitations of barium sulphate was tried in each of the above cases. The following are the records of the experiments:

I. Copper was precipitated by sodium carbonate, an excess of barium chloride was added to the hot mixture, and then an excess of hydrochloric acid was added to dissolve the copper precipitate. The barium sulphate was digested with the acid solution about half an hour, and then collected and treated as usual. The results are among those given below and are numbered 1 and 2.

II. Copper was precipitated by adding caustic potash; the rest of the treatment was as in I. The results are numbered 3 and 4.

III. Copper was precipitated by adding the solution containing it to an excess of caustic soda ; the rest of the treatment was as in I. The results are numbered 5 and 6.

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[1] Ztschr. anorg. Chem., 19, 99.

Number of analysis.	Weight of salt taken for analysis. Gram.	Weight of SO_4 found. Gram.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $CuSO_4 + 4NH_3 + H_2O$.
1	0.2611	0.1068	40.91	39.06
2	0.2548	0.1047	41.11	
3	0.2642	0.1052	39.83	
4	0.2757	0.1087	39.44	
5	0.2135	0.0847	39.67	
6	0.2088	0.0832	39.84	

In our opinion the method of Küster and Thiel is not applicable in the presence of copper.

II. Preparation of the Salt $CuSO_4 + 4NH_3 + H_2O$.

(*A*) ***Berzelius' Method.***—The preparation of this salt is said to have been described first by Stisser.[1] Berzelius, however, was the first to assign a formula to it. The method of preparation advised by him consists in treating a solution of copper sulphate with an excess of ammonia water and adding alcohol to the resulting purple solution. If the alcohol be carefully poured upon the purple solution, crystals of the salt form at the surface of contact of the two liquids. If the alcohol be slowly added and mixed with the purple solution, the salt separates as a pulverulent crystalline deposit.

We have found that in any case the salt is very unstable after it is removed from its mother-liquor. Only small quantities of it can be dried between filter-papers or on unglazed porcelain plates without considerable decomposition. This decomposition is clearly indicated by the odor of ammonia above the salt. The following are analyses of small quantities of the salt dried thus as quickly as possible :

	Weight of salt taken for analysis. Grams.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
I.	1.1978	0.3296	27.51(T)[2]	27.75
II.	0.6519	0.1797	27.57(T)[2]	

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[1] 1693. See Roscoe and Schorlemmer, II., 1, 339.

[2] All experiments and analyses made by E. E. Taylor will be marked (T).

If larger quantities are dried, even though they are first washed with absolute alcohol, the decomposition has time to go much further, as is seen from the following analyses of a specimen of perhaps 30 grams:

Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.4979	0.1298	26.07(T)	27.75
0.5022	0.1326	26.50(T)	
0.4852	0.1245	25.66(T)	

If the salt is prepared in large crystals, as it readily can be, and the surfaces of these are quickly dried with filter-paper, a pure product is not obtained because the mother-liquor is occluded in large amounts by the crystals.

Bouzat prepared crystals of this salt for use in his calorimetric studies, by cooling a hot concentrated solution of it and quickly drying the crystals that separated between filter-paper. His methods of analysis are not described in his paper, but the analyses for ammonia of his preparation gave results surprisingly like those we obtained by analyzing the same salt dried in the same way, but known by us to have partly decomposed in the drying. He found for ammonia, 26.25 and 26.45 per cent.[1] He ascribes to the salt the formula $CuSO_4 + 4NH_3 + 3/2H_2O$, which represents a salt containing 26.77 per cent ammonia.

The analysis given by Berzelius is as follows:

	Calculated for $CuSO_4 + 4NH_3 + H_2O$.	Found.
CuO	32.37	32.22
SO_3	32.55	32.58
NH_3	27.75	27.89
H_2O	7.33	7.31
	100.00	100.00

Though the pure salt cannot be prepared by drying between filter-papers, apparently it can be prepared in some other way.

We prepared a quantity of the salt by Berzelius' method and quickly transferred specimens of it from its mother-liquor to unglazed porcelain plates, in desiccators. The desiccators contained, respectively, calcium chloride, sulphuric acid, solid potassium hydroxide, and a small vessel of strongest ammonia water, and lime. In the first and second desiccators the salt soon became opaque in spots on its surface. In the third, the crystals seemed to change only in color, though it was found later that they were losing weight slowly at the same time. In the fourth desiccator (over lime), no change in the salt could be seen.

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[1] *Loc. cit.*, p. 356.

The steady loss in weight of the crystals over potassium hydroxide and ammonia water was observed for two weeks. Several of the crystals were then analyzed for ammonia with the following results :

Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.4989	0.1395	27.97(T)	27.75
0.4895	0.1372	28.03(T)	

Under these conditions the salt had apparently taken up more ammonia. We have studied this change in the salt further and will refer to it later (p. 268). Kohlschütter has since[1] used this same method for drying the cuprammonium salts used in his investigations. Reference to his paper will show that his analytical results for ammonia are also high.

The crystals dried over lime soon ceased to change in weight. Some of the salt thus dried was finely ground and put in a vacuum over lime ; it was weighed at intervals with the following results :

	Gram.
Original weight	0.6736
Weight after 13 hours	0.6733
Weight after 40 hours	0.6733

We then prepared more of the salt by Berzelius' method, precipitating it as a crystalline powder. This was dried over lime and analyzed for copper and ammonia with the following results :

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[1] Ber. d. chem. Ges., 37, 1153–70 (1904).

	Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
I. Cu	0.6918	0.1785	25.80(T)	25.86
	0.4882	0.1573	25.73(T)	
	0.4888	0.1581	25.84(T)	

	Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
II. NH_3	0.3098	0.0860	27.76(T)	27.75
	0.4184	0.1161	27.75(T)	
	0.4184	0.1157	27.65(T)	

These analyses of the purple cuprammonium sulphate are in accord with that by Berzelius, upon which the formula $CuSO_4 + 4NH_3 + H_2O$ is based.

(*B*) *Mallaert's Method.*—The method suggested by Mallaert[1] for the preparation of the salt $CuSO_4 + 4NH_3 + H_2O$ consists in the action of ammonia gas on solid $CuSO_4 + 5H_2O$. We observed a very rapid change to purple color when finely ground copper sulphate was put in a desiccator over ammonia water. This promised to be a convenient method for the preparation of the salt $CuSO_4 + 4NH_3 + H_2O$, provided the purple product is of this composition.

"Pure" copper sulphate was recrystallized five times from water and its purity assured by the following analyses of the (air-dried) product :

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 5H_2O$.
0.4404	0.1121	25.47	25.47
0.4267	0.1087	25.47	
0.3598	0.0915	25.44	

Specimens of this salt were weighed into porcelain boats and the boats put into glass tubes in a current of air that had first bubbled through ammonia water (sp. gr. 0.09). The boats were frequently transferred rapidly to well-ground glass-stoppered weighing-tubes and weighed. The following were the results :

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[1] Jour. de Pharm. d'Anvers, 1848, 217; Jsb. (Svanberg), 30, 119 (1851).

Time in minutes.	Weight of specimen.		Changes in weight.	
	I.	II.	I.	II.
	Grams.	Grams.	Gram.	Gram.
0	2.0622	1.5436		
15	2.3575	1.8485	+0.2953	+0.3049
40	2.4628	1.8994	+0.1053	+0.0509
55		1.9035		+0.0041
60	2.5170		+0.0442	
85	2.5261	1.8912	+0.0991	—0.0123
105	2.5238		—0.0023	
135	2.4911(T)		—0.0327	
150		1.8608(T)		—0.0304

The weighings were continued for half a day longer and showed continued losses. At the end of that time the specimens were about 0.3 gram heavier than the original $CuSO_4 + 5H_2O$. The above figures show maxima corresponding to gains in weight of 22.5 and 23.2 per cent, respectively. A gain of 24 per cent would represent the addition of 3 molecules of ammonia to each molecule of $CuSO_4 + 5H_2O$. Such addition-products have been described, especially in connection with the action of hydrochloric acid on copper sulphate ;[1] for example, $CuSO_4 + 5H_2O + 3HCl$.

Whatever may be the case in other instances, the products here are mixtures, as was clearly shown by the mixed colors of the contents of the boats after drying over lime. The colors ranged from sky-blue to purple. The action by which the colored mixtures are produced is accompanied by considerable evolution of heat.

To avoid the mechanical retention of much water on the surface of the salt (as was the case in the glazed porcelain boats), and to allow sufficient time for the action to complete itself, pure copper sulphate was next placed on an unglazed porcelain plate in a desiccator containing ammonia water (sp. gr. 0.9). The following analyses for ammonia were made of specimens that were dried over lime after removal from the desiccator containing ammonia water. I. was a specimen taken after three days, and II. was a specimen taken after four months:

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[1] Latschinoff : J. Russ. Phys. Chem. Soc., 1888, pp. 586, 657, 707. Jsb., 1, 621 (1888) ; 1, 517 (1889).

	Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
I.	0.3577	0.0962	26.93	27.75
II.	0.4305	0.1191	27.70	
	0.4594	0.1278	27.82	

From the analyses of II. it might be inferred that the final product of the action of ammonia gas on pentahydrated copper sulphate is $CuSO_4 + 4NH_3 + H_2O$, as was stated by Mallaert. This was disproved in two ways; first, by the analyses of II. for copper, and second, by the fact that II. was not completely soluble in water but left a green insoluble residue. The analyses for copper resulted as follows:

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.2945	0.0769	26.13	25.87
0.3227	0.0843	26.13	

We conclude that the product of the action of ammonia gas on pentahydrated copper sulphate is not the salt

$$CuSO_4 + 4NH_3 + H_2O,$$

as stated by Mallaert, and as indicated by the percentage of ammonia found in the final product, but that it is a mixture containing basic salts or copper oxide.

(*C*) *Andrae's Method.*—Andrae[1] has stated that when ammonia gas is passed into a solution of copper sulphate fine crystals of the salt $CuSO_4 + 4NH_3 + H_2O$ separate out as the concentration of ammonia in the liquid rises. Analyses are not given in Andrae's paper. This method by which the solid is produced gradually and in fine crystals is, in our opinion, the best for the preparation of the pure salt.

We prepared several hundred grams of the salt by this method and dried it over lime. We then made a complete analysis of it, and have used it as the basis for the rest of our work. The following results were obtained in its analysis:

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[1] Compt. rend., **100**, 1138.

Constituent determined.	Weight of salt taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 4NH_3 + H_2O$.
Cu	0.3543	0.0916	25.86	25.86
	0.4790	0.1239	25.87	
	0.5120	0.1325	25.88	
	0.4907	0.1268	25.84	
SO_4	0.3378	0.1324	39.19(T)[1]	39.06
	0.2631	0.1026	39.00(T)	
	0.3100	0.1212	39.09(T)	
	0.3383	0.1322	39.08(T)	
NH_3	0.4419	0.1220	27.61(T)	27.75
	0.3927	0.1092	27.80(T)	
	0.5358	0.1488	27.77(T)	
	0.3833	0.1067	27.84(T)	
H_2O	0.6691	0.0494	7.38[2]	7.33
	0.5701	0.0417	7.31	
	1.2860	0.0944	7.34	
	0.5967	0.0438	7.34	

Specimens taken from this quantity of salt were used in all of the subsequent experiments involving $CuSO_4 + 4NH_3 + H_2O$ described in this paper.

III. Properties of the Salt $CuSO_4 + 4NH_3 + H_2O$.

The dry salt is odorless. However, ammonia is given off by it instantly when it is moistened, and very soon when it is exposed to the air. It is perfectly stable when kept in a closed space over lime, as is proven by the following analyses of a specimen taken from that quantity, the complete analysis of which has just been given. This specimen had been kept over lime one year:

Constituent determined.	Weight of salt taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 4NH_3 + H_2O$.
Cu	0.4102	0.1060	25.85	25.86
	0.5012	0.1297	25.87	
	0.5209	0.1348	25.88	
NH_3	0.4766	0.1322	27.74	27.75
	0.5006	0.1393	27.82	
	0.3806	0.1057	27.77	

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[1] Determined by method described on page 260.

[2] Determined by method described on page 256.

The dry salt is not stable in a vacuum over concentrated sulphuric acid, as is shown by the following weighings of a finely ground specimen of it that was treated in this way :

	Gram.
Original weight	0.4371
Weight after twenty-four hours	0.4355
" " fifty-two "	0.4328
" " three hundred and sixteen hours	0.4144

The salt dissolves readily in small quantities of water, giving perfectly clear solutions. Its solubility in water between 21° and 22° C. was determined by sealing a quantity of the salt in a glass tube with a quantity of water that was not sufficient to dissolve it, and shaking the tube four hours. The contents of the tube were centrifuged after the shaking was complete and before the tube was opened. Two weighed quantities of the clear liquid then taken from above the crystals in the tube, by means of a pipette, were evaporated to dryness and analyzed for copper. The results were as follows :

Weight of solution analyzed. Grams.	Weight of Cu_2S found. Gram.	Weight of Cu_2S yielded by 1 gram of solution.
2.2723	0.2252	0.0991
1.4955	0.1481	0.0990

The corresponding weight of the salt $CuSO_4 + 4NH_3 + H_2O$ that was dissolved by 100 grams of water at 21° to 22° C. was 18.05 grams.

The salt takes up ammonia in a desiccator over sticks of potassium hydroxide and a very little ammonia water. This has been proven already on page 263. In this first experiment, however, the analyses were made after the salt had been exposed thus for only about two weeks. Latschinoff has stated that the molecule of water in the salt $CuSO_4 + 4NH_3 + H_2O$ is replaced by a molecule of ammonia, in an atmosphere of dry ammonia. In another experiment, therefore, we kept this salt over sticks of potassium hydroxide and a few drops of concentrated ammonia water for four months before the following analyses of the resulting product were made :

Constituent determined.	Weight of salt taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 5NH_3$.
NH_3	0.4513	0.1558	34.52	34.83
	0.3517	0.1217	34.59	
Cu	0.3638	0.0946	26.01	25.97
	0.4145	0.1079	26.02	

The salt had not lost its crystalline form in the four months. Its color had become less purple (bluer) than it was originally.

The analyses show that under the stated conditions ammonia had entered the molecule of the salt in the place of water; they show in addition to this, however, that the reaction is not a clean one, resulting in the formation of the compound $CuSO_4 + 5NH_3$, but one giving rise to mixed products containing basic salts or copper oxide.

IV. Behavior of the Salt $CuSO_4 + 4NH_3 + H_2O$ at Elevated Temperatures.

Kane has stated that when the salt $CuSO_4 + 4NH_3 + H_2O$ is heated at a temperature not above 149° C. it loses one-half of its ammonia and all of its water, and that the residue is an "apple-green powder" of the composition $CuSO_4 + 2NH_3$; that at temperatures not above 203° C. one-half of the remaining ammonia is lost, giving a residue of the composition $CuSO_4 + NH_3$; and that at 260° C. all of the ammonia is driven off and anhydrous copper sulphate remains.

In Kane's memoir there are the results of only three experiments upon this subject, and these we tabulate :

Weight of salt heated. Grams.	Weight of residue. Grams.	"Parts in 100" of residue.	Percentage loss in weight by heating.	Percentage loss calculated if $CuSO_4 + 2NH_3$ is residue.
1.969	1.545	78.47	21.53	21.20
4.921	3.854	78.32	21.68	
5.042	3.921	77.77	22.23	

In this connection Kane says: "The calculated percentage composition of ammoniacal copper sulphate is:

SO_3	32.58
CuO	32.22
$2NH_3$	27.89
HO	7.31
	100.00

which is evidently transformed by heat into

$CuO.SO_3$	64.80	HO	7.31
NH_3	13.95	NH_3	13.94
	78.75		21.25

Thus it is demonstrated by experiment that by the first action of heat all of the water and half of the ammonia is driven off, and that the green residue consists of copper sulphate united with one equivalent of ammonia. * * * I have tried to separate the water without loss of ammonia by the most careful management of the flame, but could not."

It is surprising that there is in the memoir no other evidence than this of the formation and composition of what are announced by Kane to be new compounds. As has already been pointed out, losses in weight cannot be relied upon to differentiate water from ammonia. Thus, if three-fourths of the ammonia had separated from the salt at 149° C., instead of half of it and all of the water, the loss in weight would have been 20.81 per cent instead of 21.20 per cent. It is true that Kane proved in some way, to his own satisfaction, that water is given off with the ammonia, but how he determined that *all* of the water is given off it is impossible to say. We shall show later that the same salt as that with which he was working when heated to 100° C. instead of 149° C. loses on the average 21.12 per cent. This percentage loss differs less from the 21.20 per cent that was his standard of reference than do his own experimental results, yet at 100° C. the salt (we shall show) loses more than half of its ammonia and probably retains a little of its water.

In discussing the change in the salt $CuSO_4 + 4NH_3 + H_2O$

at 203° C., Kane gives no figures and no description of the product.

(*A*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 149° C.*—We fitted out a copper air-bath with a Reichert gas-regulator so that the temperature in the bath could not rise above 149° C. We heated a specimen of the pure $CuSO_4 + 4NH_3 + H_2O$ in this bath for two hours. The product was an "apple-green powder." The following results were obtained when this product was analyzed for ammonia:

Weight of powder taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 2NH_3$.
0.6815	0.1130	16.58(T)	17.61
0.6522	0.1080	16.56(T)	
0.6516	0.1076	16.51(T)	

Another quantity of the pure salt $CuSO_4 + 4NH_3 + H_2O$ was then heated in a Victor Meyer bath containing a fraction of illuminating oil boiling between 144° and 147° C. After a few hours the product was removed and analyzed for ammonia and copper. It is interesting to note that the product was again of an "apple-green" color, and that it was of a different shade of green from that produced in the former experiment. The analytical results were as follows:

Constituent determined.	Weight of powder taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 2NH_3$.
NH_3	0.5085	0.0861	16.93(T)	17.61
	0.5087	0.0863	16.96(T)	
	0.4840	0.0822	16.98(T)	
Cu	0.4597	0.1513	32.92	32.82

The insufficiency of Kane's data is emphasized by these experiments. The "apple-green powders" were mixtures whose uniformity depended upon the fact that they were stirred thoroughly during the heatings. Their composition is not even approximately represented by the formula

$$CuSO_4 + 2NH_3.$$

No more direct way to find out just what takes place when the salt $CuSO_4 + 4NH_3 + H_2O$ is heated at 149° C. suggested itself than to heat weighed quantities of the pure salt under such conditions that all the water and ammonia evolved by it could be collected separately and weighed, and the residue weighed. The apparatus used for this purpose has been described on page 256. The results of four experiments, lasting two hours each, were as follows :

Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight during heating.	Weight of water collected during heating.	Percent'ge weight lost by salt as water.	Weight of ammonia collected during heating.	Percent'ge weight lost by salt as ammonia.
Gram.	Gram.		Gram.		Gram.	
0.6691	0.5255	21.46	0.0494	7.38	0.0953	14.24
0.5701	0.4481	21.39	0.0417	7.31	0.0807	14.15
0.5846	0.4597	21.37	0.0431	7.37	0.0828	14.16
0.5260	0.4135	21.39	0.0388	7.38	0.0745	14.16

Calculated percentage loss in weight when $CuSO_4 + 4NH_3 + H_2O$ is converted into $CuSO_4 + 2NH_3 = 21.20$.

Calculated percentage of water in the salt $CuSO_4 + 4NH_3 + H_2O = 7.33$.

One-half the calculated percentage of ammonia in the salt $CuSO_4 + 4NH_3 + H_2O = 13.8$.

Analyses of the residues for ammonia resulted as follows :

Weight of residue taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 2NH_3$.
Gram.	Gram.		
0.2379	0.0417	17.48(T)	17.61
0.3182	0.0552	17.35(T)	

These experiments show that even when the salt $CuSO_4 + 4NH_3 + H_2O$ is decomposed in dry air at 149° C. the product is not a definite chemical compound but a mixture that approximates in composition to the formula $CuSO_4 + 2NH_3$. This mixed product has a pale-blue color, in no way like the "apple-green" color of the products in the previous experiments.

(*B*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 125° C.*—A recent paper by Sabbatani that was available to us only in abstract[1] states that at temperatures from 120° to 125° C. both of the salt $CuSO_4 + 4NH_3 + H_2O$ and $CuCl_2 + 4NH_3 + H_2O$ lose half of the ammonia and all of the water they contain. The abstract gives no details. We carried out experiments with specimens of the first of these two salts at 120° to 125° C. in the same apparatus as those at 149° C. The results were as follows:

Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight during heating.	Weight of water collected during heating.	Percent'ge weight lost by salt as water.	Weight of ammonia collected during heating.	Percent'ge weight lost by salt as ammonia.
Grams.	Grams.		Gram.		Gram.	
1.2860	1.0126	21.25	0.0944	7.35	0.1812	14.09
0.6195	0.4872	21.34	0.0465	7.50	0.0868	14.01
0.5967	0.4699	21.25	0.0438	7.35	0.0811	13.59
0.4099	0.3225	21.32	0.0297	7.25	0.0558	13.63

The percentage losses are less than at 149° C. and the product approaches in composition more nearly to the formula $CuSO_4 + 2NH_3$. The color differed very little from that of the product at 149° C., being slightly bluer.

(*C*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 100° C.*—We noticed that this salt is decomposed also at 100° C. When heated in dry air at 100° C. a product having constant weight is finally obtained. The following results show this, and, incidentally, the accuracy associated with all the experiments in this paper that involve the weighing of boats and residues:

		Grams.
(6)	Total weight (tube, boat, and residue)	10.39500
	Weight after twelve hours more at 100° C.	10.39358
	" " twenty " " " " "	10.39359
	" " thirty-six hours more at 100° C.	10.39351
(7)	Total weight (platinum boat and residue)	1.16791
	Weight after three hours more at 100° C	1.16791
(8)	Total weight (platinum boat and residue)	1.21362
	Weight after six hours more at 100° C.	1.21363

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[1] Jsb., 1, 96 (1897); Ann. Chim. Pharm., 26, 337.

Repeated experiment showed that the losses in weight are not always the same. This is readily seen from the following figures:

Number of experiment.	Weight of salt heated. Gram.	Weight of residue after heating. Gram.	Percentage loss in weight.
1	0.4894	0.3878	20.75(T)
2	0.4564	0.3606	20.99
3	0.4164	0.3273	21.39(T)
4	0.4664	0.3669	21.33
5	0.4332	0.3410	21.28(T)
6	0.4184	0.3300	21.24

The analyses of the products in these experiments indicated that they were of varying composition:

Constituent determined.	Weight of residue taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.
NH_3	0.8167	0.1358	16.62(T)
	0.2201	0.0368	16.72(T)
	0.1911	0.0324	16.83(T)
	0.2393	0.0394	16.48(T)
Cu	0.2311	0.0741	32.07
	0.1873	0.0602	32.18
	0.2215	0.0896	32.23

Latschinoff has stated that when hydrochloric acid is led over pentahydrated copper sulphate at room temperature there results by degrees the compound $CuSO_4 + 5H_2O + 3HCl$, and by further action the compound $CuSO_4 + 2H_2O + 2HCl$, which breaks down when air is led over it into $CuSO_4 + H_2O + \frac{1}{8}HCl$. This $\frac{1}{8}HCl$ cannot be removed by a stream of air. He has also stated that when the compound $CuSO_4 + 5NH_3$ is heated under certain conditions the final product is $CuSO_4 + \frac{1}{4}NH_3$. Evidence of this kind is of especial interest as bearing upon the molecular weight of (solid) copper sulphate. At first we believed that the residue we obtained at 100° C. might be classed with these interesting compounds. Thus, if the product was fairly represented by the formula $CuSO_4 + 1\frac{7}{8}NH_3 + \frac{1}{8}H_2O$ it would be formed from the salt $CuSO_4 + 4NH_3 + H_2O$ by a loss of 21.15 per cent, and it would contain 16.50 per cent ammonia and 32.79 per cent copper. The experimental results that have been given do not quite agree with these calculated values, but approximate to them. This might be due to the water evolved from some of the salt acting upon those, or other, parts of the specimen producing mixed products. To avoid this as far as possible we heated very small quantities of pure $CuSO_4 + 4NH_3 + H_2O$, carefully spread out in thin layers on the bottom of a thin platinum boat. This boat was used to distribute better the error in weighing. The following results were thus obtained :

Number of experiment.	Weight of salt heated. Gram.	Weight of residue after heating. Gram.	Percentage loss in weight.
7	0.0682	0.0537	21.21
8	0.1261	0.0996	20.96
9	0.1112	0.0877	21.08
10	0.1746	0.1377	21.15
11	0.1617	0.1276	21.09
12	0.2644	0.2085	21.12

Several of the residues were analyzed :

Number of experiment.	Constituent determined.	Weight of residue taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage of constituent calculated for $CuSO_4 + 2NH_3$.
9	Cu	0.0870	0.0281	32.29	32.82
10		0.1373	0.0447	32.58	
11		0.1275	0.0418	32.76	
12	NH_3	0.2084	0.0365	17.49	17.61

These results are not in agreement with the formula we have tentatively assumed. If the product could be correctly represented by the formula $CuSO_4 + 1\frac{3}{4}NH_3 + \frac{1}{4}H_2O$, its formation should be preceded by a loss in weight of 21.12 per cent, whereas the average of these last six experiments is 21.10 per cent. But this formula requires 15.39 per cent ammonia.

It is not possible to find any one formula to fit all the data at hand. Whatever may be the case in other instances, our experiments leave no doubt that at 100° C. $CuSO_4 + 4NH_3 + H_2O$ yields a mixed residue.

We believe that the action of water is responsible for the production of these mixtures. We tested this by heating the salt $CuSO_4 + 4NH_3 + H_2O$ at 100° C. in a bath where the vapor of water had access by free diffusion to the heated material. The material in the bath was stirred frequently, and specimens for analysis were taken from it at intervals of about twelve hours. The following were the results:

Number of analysis.	Weight of residue taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.
I.	0.4795	0.0767	15.99(T)
II.	0.3571	0.0514	14.37(T)
	0.4461	0.0642	14.39(T)
III.	0.3698	0.0538	14.54(T)
	0.7507	0.1100	14.65(T)
IV.	0.2948	0.0413	14.01(T)
	0.4869	0.0682	14.01(T)

It is interesting to note that the specimens, the analyses of which have just been given, were all "apple-green" in color.

The behavior of the salt $CuSO_4 + 4NH_3 + H_2O$ when heated in dry air at 100°, 125°, and 149° C. seems to be characteristic of salts whose molecules contain copper sulphate combined with water. We have found it impossible to prepare pure $CuSO_4 + H_2O$ and $CuSO_4$ from the pentahydrate by heating it in dry air.

In dehydrating the pentahydrate at 100° C. we used an air-bath consisting of a large glass tube encased in a tin condenser-jacket, through which steam was passed. The following is the record of an experiment in which some of the pure pentahydrated copper sulphate, the analysis of which has been given on page 264, was heated in this air-bath in a current of dry air:

	Gram.
Weight of pentahydrate taken	0.7629
" after five hours heating	0.5441
" " four hours more	0.5440
" " six " "	0.5441
" " three " "	0.5442
" " one hour at 105° C.	0.5441
" " three hours at 105°–110° C.	0.5441

The percentage loss in weight was 28.69 per cent, whereas the calculated percentage loss in weight when $CuSO_4 + 5H_2O$ decomposes into $CuSO_4 + H_2O$ is 28.85 per cent. The material in the boat, after heating, was brownish all over the surface and pale-blue beneath the surface. We then heated another specimen of the pentahydrate in a Victor Meyer bath, using alcohol in the bath. When the residue had become constant in weight at 78° C. it was found to have been formed from the pentahydrate by a percentage loss in weight of 28.55 per cent; calculated, 28.85 per cent. This residue was tinged with brown, and when heated in dry air at 100° C. it became decidedly brownish.

Several attempts to prepare anhydrous copper sulphate from the pentahydrate by heating it in dry air at the lowest temperature given by Graham[1] (220° C.) resulted similarly in browned products and varying losses in weight, as is shown by experiments I. to III. in the following:

Number of experiment.	Weight of pentahydrate heated. Grams.	Weight of residue after heating. Gram.	Percentage loss in weight found.	Percentage loss in weight calculated.
I.	0.4416	0.2839	35.71(T)	36.69
II.	0.6185	0.3961	35.95(T)	
III.	0.3974	0.2533	36.26(T)	
IV.	1.1253	0.7199	36.03	
V.	1.1067	0.7084	35.99	

Experiments IV. and V. were carried out by heating to constant weight at 280° C.

In view of these experiments, we are of the opinion that a molecule containing copper sulphate combined with water cannot undergo change without secondary reactions taking place between the water and the copper sulphate, giving mixed products. By this view the behavior of the salt $CuSO_4 + 4NH_3 + H_2O$ when heated in dry air at 100°, 125°, and 149° C. is readily explained, as well as our experiences in dehydrating pentahydrated copper sulphate. That mixed products are always formed in this dehydration we find also very clearly shown by the experiments of Naumann,[2] the view as readily accounts for the failure of Mallaert's method for the preparation of the salt $CuSO_4 + 4NH_3 + H_2O$, and for the fact that basic salts are formed when ammonia acts on the salt $CuSO_4 + 4NH_3 + H_2O$.

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[1] Ann. Chem. (Liebig), 20, 147.

[2] Ber. d. chem. Ges., 7, 2, 1573.

(*D*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 203° C.*—We heated at 200° to 203° C. residues previously obtained at 125° and 149° C. We used the same bath as was used in the experiments at 125° and 149° C., but provided it with a Reichert gas-regulator so arranged that the mercury in it closed an electric circuit and rang a bell as soon as the temperature reached 202° C. In the two following experiments the residues were heated about eight hours before their weights became constant:

Original weight of salt heated. Gram.	Weight of of residue after heating. Gram.	Percentage loss in weight.	Percentage loss calculated if $CuSO_4 + NH_3$ is formed.
1.0788	0.7739	28.26	28.15
0.5498	0.3944	28.25	

The following weighings of the second product prove that its weight was constant for the given conditions:

	Gram.
Weight of salt before heating	0.5498
" after twenty hours at 200°–203° C.	0.3945
" " thirty-nine hours at the same temperature	0.3944

As would be expected, the results show that the product is not a definite chemical compound.

In the above experiments the appearance of the products was perfectly uniform, and their color light-blue, but in other experiments at the same temperature, in which the heating was not even throughout the length of the boat, mixtures of substances with colors from sky-blue to pale-green and having perfectly constant weight, were obtained. The following description of one such experiment illustrates the course followed in raising the temperatures and also the constancy in weight of the mixed residues in these experiments:

Heated two hours at 125° C.
" five hours below 130° C.
" four hours at 155° to 170° C.
" three hours at 170° to 190° C.
" two hours at 200° to 203° C.

	Gram.
Weight of residue was then	0.3032
Heated four hours at 200° to 203° C.	
Weight of residue	0.3030
Heated three hours at 200° to 203° C.	
Weight of residue	0.3030
Original weight of $CuSO_4 + 4NH_3 + H_2O$ was	0.4196

Percentage loss in weight, 27.79

In four such experiments entirely similar mixed products were obtained, the losses in weight ranging from 27.09 to 27.79 per cent.

(*E*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 260° C.*—Kane has stated that anhydrous copper sulphate is formed when this salt is heated at 260° C. We tried several such experiments, all of which yielded brown products. The following analyses of three of these products for copper show that they were not anhydrous copper sulphate :

Percentage of copper found in residue.	Percentage of copper calculated for $CuSO_4$.
39.51	39.83
40.13	
39.51	

V. Properties of Aqueous Solutions of the Salt $CuSO_4 + 4NH_3 + H_2O$.

1. All solutions of the salt have quite a strong odor of ammonia. The tension of ammonia over a solution of copper sulphate, to which an excess of ammonia has been added, is less than over an aqueous solution of ammonia of the same concentration. If the tension in a given case be corrected by subtracting from the total tension that due to 4 gram-molecules of ammonia for every gram-atom

of copper present, the corrected tension is less than that actually observed. Locke and Forssell have recently[1] interpreted this excess of tension as due to the lesser solubility of ammonia in cuprammonium sulphate solutions than in water. They assume that the complex cuprammonium salt and the complex cuprammonium ion do not affect the tension at all by their dissociation.

It is true that if the salt underwent any considerable molecular dissociation with loss of ammonia, we could not have kept it in a bell-jar over lime for more than a year without decomposition (see page 267), and it would lose weight in a vacuum over sulphuric acid much faster than we found that it did (see page 268). On the other hand, the facts that the salt smells strongly of ammonia at once when moistened, that the decomposition by water is so rapid that the salt cannot be dried between filter-papers, and that all of its solutions smell strongly of ammonia, are not in accord with their assumption. There is sufficient reason in these facts to believe that the excess tension of ammonia is due at least in part to the hydrolytic dissociation with loss of ammonia of the complex salt or its electrolytic dissociation-products.

2. The salt gives a clear solution when water is poured gradually upon it, but if the addition of water is continued a permanent precipitate is formed at about N/20 to N/25[2] concentration. When a solution of the salt is dropped into water a permanent precipitate is formed at once.

3. A N/10 solution of the salt after standing a couple of days in a tightly closed vessel begins to deposit a crystalline blue solid ; this continues for weeks.

4. If a current of air (free from carbon dioxide) is passed through a N/10 solution of the salt, ammonia is removed by the air, and after about twenty-four hours a finely crystalline blue deposit begins to form on the walls of the vessel. This precipitate increases in bulk throughout a long period of time.

5. When a solution of the pure salt, or of the pure salt with

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[1] This JOURNAL, 31, 268 (1904).

[2] These concentrations are fractions of "molecular normal."

an excess of ammonia, is titrated into acids the precipitate at first formed redissolves until a definite limit is reached, when the precipitate becomes permanent. This point at which the precipitate becomes permanent is very sharp, and in a solution of the pure salt lies very close to the point of neutrality of the liquid. This point is also independent of the anion of the acid used, at least in the case of strong acids. The following figures present a comparison of the weights of different acids used up by 1 cc. of a given salt solution with the weights of the same acids calculated as just equivalent to the ammonia of the salt in 1 cc. of the given solution. They also show that the nature of the anion of the acid is without effect.

	Calculated. Gram.	Found. Gram.
HCl	0.0147	0.0146
H_2SO_4	0.0198	0.0192
HNO_3	0.0255	0.0252

6. Pure copper sulphate is very approximately neutral to methyl orange indicator. This indicator can be used to determine the alkalinity of the liquids in which the permanent precipitate described in (5) is formed. The following results show the definiteness of the methyl orange end-reaction under these conditions, as well as that of the reaction indicated by the permanent precipitate. They also show that the precipitate forms in a feebly alkaline solution :

Volume of acid required by 1 cc. cuprammonium solution to give permanent precipitate. cc.	Volume of acid required by same to give neutrality to methyl orange. cc.
1.93	1.98
1.94	1.98
1.94	1.98
2.32	2.38
2.32	2.38
2.33	2.38
3.03	3.12
3.04	3.11
3.04	3.11

7. The reaction indicated by the permanent precipitate is affected by the presence of ammonia, as is also the neutralization indicated by methyl orange. In neither case is the effect proportional to the ammonia added. The following results set forth these points :

Number of solution.	Molecular concentration of solution with respect to copper.	Ratio Cu : NH_3 in solution.	Ratio Cu : $\overset{+}{H}$ at time of permanent precipitation.	Ratio Cu : $\overset{+}{H}$ at time of neutrality to methyl orange.
I.	N/9.87	1 : 4	1 : 3.88	1 : 3.97
II.	N/9.95	1 : 4.82	1 : 4.65	1 : 4.77
III.	N/9.55	1 : 6.06	1 : 5.84	1 : 5.99

8. In a given solution both of these reactions change with time. The total alkalinity diminishes and the alkalinity, at the moment when the permanent precipitate is formed, increases. The presence of an excess of ammonia does not prevent this displacement of the two end-reactions with time. Thus after solution I., above, had deposited some of the blue solid mentioned in (3) the alkalinity at the moment of permanent precipitation had increased from 0.09 to 0.12 gram-equivalents of $\overline{OH}$ to each gram-equivalent of copper present. The following results show the changes with time in solution III., above. The time was forty-eight hours. They also show that the excess of ammonia present did not stop these changes :

Number of solution.	Concentration with respect to copper.	Ratio Cu : NH_3 in the solution.	Ratio Cu : $\overset{+}{H}$ at time of permanent precipitation.	Ratio Cu : $\overset{+}{H}$ at time of neutrality to methyl orange.
III.	N/9.55	1 : 6.06	1 : 5.84	1 : 5.99
III.	N/9.55	1 : 6.06	1 : 5.80	1 : 5.96

These experiments were conducted with the greatest care. The flasks were carefully calibrated by weighing the water they contained at definite temperatures, and the burettes were calibrated by a method devised recently by one of us.[1] The solutions were made by weighing the flasks first dry and empty, and again after the salt had been introduced and the flasks stoppered. Significant differences in temperature were corrected for.

The properties of solutions of the salt $CuSO_4 + 4NH_3 + H_2O$ indicate that the salt is decomposed by water with the partial separation of ammonia from the combination in which it is held by the salt in the dry condition (see 1, 2, and 3 above). This decomposition is probably an hydrolysis (see 6). In solutions of the pure salt it proceeds at least as far as the formation and precipitation of basic salts (see 2, 3, and 5). In solutions of the salts, even though they may contain an excess of ammonia, the concentration of hydroxyl ions undergoes changes throughout a considerable period of time (see 8). These changes are hastened or retarded by the removal or addition of ammonia (see 4 and 7), but the effects of the ammonia do not bear any simple relation to the concentration of the ammonia (see 8).

The formula $CuSO_4 + 4NH_3 + H_2O$ does not correctly represent the salt. If this formula were correct, the addition of 1 molecule of the salt to 4 equivalents of acid would produce a clear solution containing copper sulphate and ammonium salts and the products of their electrolytic dissociation, and would not produce a permanent precipitate (see 5).

VI. Summary.

1. We have shown the method of Fresenius and the "suggestion" of Küster and Thiel to be unreliable in the quantitative separation of sulphuric acid from copper. We have described a satisfactory method for the separation and for the determination of ammonia and water in a mixture of the vapors of the two. The conditions under which reliable results can be obtained in the complete analysis of cuprammonium sulphates have been worked out and have been stated.

2. The preparation of the salt $CuSO_4 + 4NH_3 + H_2O$ has been described, and a method of drying it and keeping it in-

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[1] This JOURNAL, 30, 96 (1903).

definitely in an analytically pure condition has been given. Its composition has been proved by complete analyses. Other products described as this cuprammonium sulphate by Mallaert and Bouzat have been shown to be mixtures. The method of drying hydrated cuprammonium salts over sticks of potassium hydroxide and a very little ammonia water, used recently by Kohlschütter, has been shown to alter the composition of the salts.

3. The properties of the pure dry salt $CuSO_4 + 4NH_3 + H_2O$ have been studied, and it has been shown that its molecular dissociation with loss of ammonia must be very slight. Its solubility at 21° to 22° C. has been determined. The action of dry ammonia upon the salt has been studied, and it has been shown that under the given conditions the replacement of the molecule of water in the salt by a molecule of ammonia described by Latschinoff does not take place without other reactions setting in, producing mixed products.

4. We have studied the behavior of the salt $CuSO_4 + 4NH_3 + H_2O$ when heated at 100°, 125°, 149°, 203°, 260° C., and have shown that the products in all cases were mixtures. The definite chemical compounds

$$CuSO_4 + 2NH_3 \quad \text{and} \quad CuSO_4 + NH_3$$

described by Kane do not exist as such ; if they are formed at all they are mixed with other products. We have studied the behavior of pentahydrated copper sulphate at 78°, 100°, 220°, and 260° C. and have shown that the dehydration-products were mixtures. We have shown that the action of ammonia on pentahydrated copper sulphate produces a mixture and that this is also true when ammonia acts on the salt $CuSO_4 + 4NH_3 + H_2O$, even though both reactions take place at ordinary temperatures. We are of the opinion that a solid compound containing both copper sulphate and water cannot undergo change without other reactions between these two constituents taking place, giving rise to mixed products. For this reason, results of experiments on record in which solid hydrated compounds of copper sulphate have been heated, or treated with a gas, or changed in other ways (while still solid) are, *ipso facto*, open to doubt. The most recent work to which this applies is that of Latschinoff.

5. Properties of aqueous solutions of the salt

$$CuSO_4 + 4NH_3 + H_2O$$

have been described that show that the system

$$\{CuSO_4 + 4NH_3 + H_2O\} + xH_2O$$

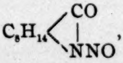
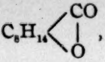
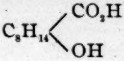
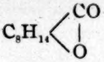
as found in a solution of the salt is in an unstable condition, beginning with its existence to undergo a change that continues for a long time and that it is in some cases not complete while the system remains homogeneous. The change which results in the precipitation of basic salts is hastened by the removal of ammonia and by great dilution. We have found that the change in the solutions can be followed readily by taking advantage of the facts that cuprammonium sulphate solutions titrated into acids give a definite end-reaction characterized by the formation of a permanent precipitate, and that copper sulphate solutions are practically neutral to methyl orange indicator. The results obtained in this way do not permit of a satisfactory interpretation.

Because of the changes in solutions of this cuprammonium sulphate that continue for a considerable time, deductions of a general character drawn from studies of cuprammonium sulphate solutions (in water) must be considered doubtful except in cases where it has been shown that the measurements were made after equilibrium had been established in the solutions. The most recent work to which this applies is that of Dawson and McCrea and of Locke and Forssell.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
April, 1904.

THE DECOMPOSITION OF NITROSO COMPOUNDS.

BY WILLIAM A. NOYES AND RENÉ de M. TAVEAU.

Bredt has stated[1] that when the nitroso derivative of the anhydride of dihydroaminocampholytic acid,  $C_8H_{14}{<}\begin{array}{l}CO\\ \mid\\ NNO\end{array}$, is decomposed by treatment with sodium hydroxide a lactone,  $C_8H_{14}\left\langle\begin{array}{l}CO\\ \mid\\ O\end{array}\right.$, is formed. Blanchard and one of us, on repeating the experiment,[1] probably with somewhat different conditions, as Bredt gives no details, obtained as the chief products of the decomposition active α-campholytic acid and dihydrohydroxycampholytic acid, with little or none of the lactone. More recently Bredt has prepared the nitroso derivative of the anhydride of aminolauronic acid and states[2] that on decomposing this with sodium hydroxide a lactone is also formed. He has, apparently, overlooked the fact that the same lactone was obtained in an impure condition by one of us[3] some years ago and called isocampholactone. In the decomposition of the lauronic acid, or its ester with nitrous acid, four products are found: Isolauronolic acid, $C_8H_{13}CO_2H$; hydroxylauronic acid,  $C_8H_{14}\left\langle\begin{array}{l}CO_2H\\ \\ OH\end{array}\right.$; isocampholactone,  $C_8H_{14}\left\langle\begin{array}{l}CO\\ \mid\\ O\end{array}\right.$; and a hydrocarbon, C_8H_{14}.

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[1] Ann. Chem. (Liebig), **314**, 392.

It seems, therefore, that dihydroaminocampholytic acid and aminolauronic acid each give two hydroxy acids on treatment with nitrous acid, and that one of each of these pairs of acids forms a lactone while the other does not. It seems of interest to determine whether the hydroxy acid which forms the lactone and the other one derived from the same amino acid which forms no lactone are stereomeric or place isomers. It was also of interest to determine whether the decomposition of the nitroso derivative of the anhydride of aminolauronic acid gives only the lactone, as seems to be implied in Bredt's statement, or if it gives also the other compounds referred to above. While our work has only been carried far enough to answer the latter question, we have incidentally discovered a new class of compounds formed when the decomposition takes place in the presence of an alcoholic solution of sodium hydroxide. The study of these compounds is far from complete, but as we can no longer continue the work together it seems desirable to publish the results already obtained.

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[1] This JOURNAL, **26**, 284.

[2] Ber. d. chem. Ges., **35**, 1291.

[3] This JOURNAL, **17**, 432.

Preparation of Camphoramidic Acids.—Considerable experience in the preparation of the camphoramidic acids has been gained since the details of preparation were last given[1] and as they furnish the starting-point for the preparation of a large number of important derivatives of camphoric acid it appears worth while to give the methods now used. One hundred grams of finely powdered camphoric anhydride are placed in a 500 cc. bottle, 150 cc. of strong ammonia (0.90) added, the stopper of the bottle firmly tied down, and the mixture shaken vigorously till the anhydride has passed into solution. The solution is then cooled rapidly, but thoroughly, and the ammonium salt of the α-camphoramidic acid, which separates, filtered off on a plate and washed twice with a small amount of a 10 per cent solution of ammonium chloride. To the filtrate from the ammonium salt is added a 50 per cent solution of sodium hydroxide, which causes the separation of a considerable amount of the sodium salt of the β-camphoramidic acid. This is filtered off on a hardened filter and washed twice with a small amount of a 10 per cent solution of sodium hydroxide. The free amidic acids are obtained by dissolving the respective salts in warm water, cooling, and precipitating with hydrochloric acid. The acid should be added very carefully, with vigorous stirring, till the amidic acid begins to separate in crystalline form. If the mineral acid is added too rapidly, the acid will separate as a gummy mass, which is less pure. The yield is 45 to 55 per cent of the α-acid and 20 to 25 per cent of the β-acid.

The hydrochloride of aminolauronic acid was prepared from the α-camphoramidic acid[2] and the anhydride was prepared by distilling the hydrochloride with lime.[3] The anhydride may also be prepared by heating the free amino acid to 300°

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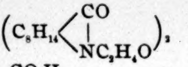
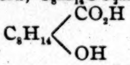
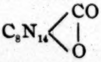
[1] This **Journal**, **16**, 502.
[2] *Ibid.*, **16**, 506.
[3] *Ibid.*, **16**, 507.

in an oil-bath. It boils at 285°. The isomer derived from dihydroaminocampholytic acid boils at 285° to 287°.[1] The rotation of a 7 per cent solution in absolute alcohol is $[\alpha]_D =$ —60°.1 at 26°.

The nitroso compound was prepared by dissolving the anhydride in dilute hydrochloric acid and adding a little more than the calculated amount of sodium nitrite.[2] The nitroso compound was crystallized from alcohol or ligroin. It melts at 138° to 139°. The racemic form also melts at 138°.[3]

When the nitroso compound is moistened with strong alcohol and a 10 per cent solution of sodium hydroxide is added, while the whole is cooled with ice-water, it decomposes with the formation of the various products in approximately the following proportion :

	Grams.
Nitroso compound taken	19.5
Hydrocarbon, C_8H_{14}	2.5
Condensation-product,  $\left(C_8H_{14}\left\langle\begin{array}{l}CO\\ \vert\\ NC_2H_4O\end{array}\right.\right)_2$	5.0
Isolauronolic acid, $C_8H_{14}CO_2H$	1.2
Hydroxy acid,  $C_8H_{14}\left\langle\begin{array}{l}CO_2H\\ OH\end{array}\right.$	1.5
Isocampholactone,  $C_8N_{14}\left\langle\begin{array}{l}CO\\ \vert\\ O\end{array}\right.$	1.3

These products were separated essentially as follows : After the decomposition of the nitroso compound was complete the mixture was heated in a current of steam, which carried over the hydrocarbon. This was easily separated from the aqueous distillate. The oily residue in the distilling-bulb sometimes solidified and consisted mainly of the condensation-product. By acidifying the alkaline solution separated from the condensation-product, the isolauronolic acid, lactone, and hydroxy acid were liberated and were then extracted from the solution with ether. After distilling the ether, the lactone and isolauronolic acid were driven over with steam, leaving the hydroxy acid behind. The lactone and isolauronolic acid were extracted from the distillate with ether, and after distilling the ether, were separated by a solution of potassium carbonate, which dissolves the acid and not the lactone.

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[1] This JOURNAL, 16, 504.

[2] Bredt : Ber. d. chem. Ges., 35, 1291.

[3] Noyes and Warren : This JOURNAL, 28, 486.

There was evidently considerable loss in the separation of the products and the results cannot be considered accurate, but it is evident that the hydroxy acid may be considered the direct product of the decomposition with as much reason as the lactone.

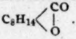
The hydroxy acid may be distilled under diminished pressure without decomposition, boiling at 180° to 185° under a pressure of 25 mm. It is evident that this is the same hydroxy acid as that whose ester is formed by the action of nitrous acid on the ethyl ester of aminolauronic acid. Hydroxydihydrocampholytic acid, the isomer which corresponds to this but which has the positions of the hydroxyl and carboxyl reversed, also forms no lactone.

Configuration of the Lactone.—It is generally assumed that in ordinary camphoric acid, which forms an anhydride, the carboxyl groups are both on the same side of the plane of the ring, while the isocamphoric acid is assumed to be the trans form. The fact that ordinary camphoric acid, dihydroaminocampholytic acid, dihydrohydroxycampholytic acid, and α-bromdihydrocampholytic acid are all dextrorotatory and that their rotatory power, except that of the last, is of much the same order of magnitude, is considerable evidence that all possess a similar configuration. If this is true and all are *cis* compounds, it seems probable that isocampholactone and the lactone derived from dihydroaminocampholytic acid are *trans* compounds. It would follow from this that cyclic hydroxy acids having carboxyl and hydroxyl in the 1,3-position form lactones only when the groups are *trans* with regard to each other. The close agreement in the specific rotation of the anhydride of aminolauronic acid and of isocampholactone indicates that these have a similar configuration, however, and the evidence is, at present, conflicting. The matter is of considerable interest, and it is our intention to give it further study. Perkin and Thorpe[1] have recently described a cyclic γ-hydroxy acid which forms no lactone, and they refer to other similar cases.

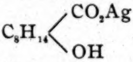
Isocampholactone.—As already stated, this was discovered by one of us some years ago, but it was obtained only in small amount and in an impure condition, so that the compound was not analyzed and the melting-point was found nearly 10° too low. Bredt gives the melting-point as 32°, and we have found the same. He gives no analyses. We found:

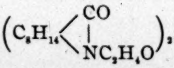
I. 0.1336 gram substance gave 0.3426 gram CO_2 and 0.1086 gram H_2O.

II. 0.1218 gram substance gave 0.3105 gram CO_2 and 0.0988 gram H_2O.

	Calculated for  $C_8H_{14}<\begin{matrix}CO\\ \vert \\ O\end{matrix}$.	Found. I.	Found. II.
C	70.11	69.93	69.53
H	9.11	9.18	9.08

The substance is laevorotatory. For a 5 per cent solution in alcohol $[\alpha]_D = -60°.7$.

The silver salt,  $C_8H_{14}<\begin{matrix}CO_2Ag\\ OH\end{matrix}$, of the hydroxy acid corresponding to the lactone was prepared by heating the latter with a little more than the calculated amount of alcoholic potash for an hour and a half, distilling off the alcohol, exactly neutralizing with nitric acid and precipitating with silver nitrate. The salt gave 38.82 per cent of silver. Calculated, 38.68 per cent.

The condensation-product,  $\left(C_8H_{14}<\begin{matrix}CO\\ \vert \\ NC_2H_4O\end{matrix}\right)_2$, is formed when the nitroso compound is moistened with alcohol and decomposed by adding an aqueous solution of sodium hydroxide, or better, by decomposing the nitroso compound by an alcoholic solution of sodium hydroxide. The substance was crystallized from alcohol and from ligroin. From the latter solvent it separates in large, well-formed plates having a faint yellow color. It melts at 104°. It is almost insoluble in water. It dissolves slightly in dilute hydrochloric acid and may be reprecipitated by ammonia, the reprecipitated substance melting still at 104°. The analysis gave:

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[1] J. Chem. Soc. (London), **85**, 131.

	Calculated for $(C_{11}H_{18}NO_2)_2$.	Found. I.	Found. II.
C	67.28	66.91	67.00
H	9.25	8.93	9.13
N	7.16	7.50	7.51

An amount weighing 0.1774 gram dissolved in 15.67 grams of benzene gave a lowering of the freezing-point of 0°.166, and 0.2445 gram gave a lowering of 0°.229. 0.1904 gram dissolved in 39.42 grams of benzene gave a rise in the boiling-point of 0°.390. These correspond to the values 334, 348, and 343 for the molecular weight. Calculated for $(C_{11}H_{18}NO_2)_2$, 392.4. The agreement is not satisfactory, but the results indicate that the substance contains a doubled molecule as compared with the original substance. It is also apparent that the ethyl alcohol used has taken part in the formation of the compound.

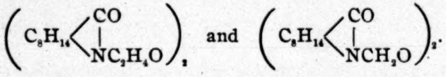
This last fact suggested the use of a solution of sodium hydroxide in methyl alcohol. When the nitroso compound is decomposed by such a solution, a similar condensation-product having the formula $(C_{10}H_{16}NO_2)_2$ is formed. This crystallizes from ligroin in leaflets, which melt at 99°. It is slightly soluble in acids and is precipitated from the solution by ammonia. The analysis gave:

	Calculated for $(C_{10}H_{16}NO_2)_2$.	Found. I.	Found. II.
C	65.86	65.87	65.57
H	8.86	8.40	8.49
N	7.70	7.69	....

A solution of 0.2311 gram in 20.68 grams of benzene gave a freezing-point lowering of 0°.160, and 0.3598 gram gave a lowering of 0°.286. These correspond to 341 and 327 for the molecular weight. Calculated, 364.3.

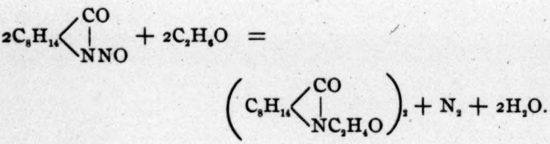
Experiments were also tried with isoamyl alcohol and with allyl alcohol. Condensation-products were evidently formed in both cases but these could not be made to crystallize.

When these formulas are examined it is seen that they correspond to the nitroso compound less the nitroso group and with the addition of a molecule of acetaldehyde or formaldehyde, thus:



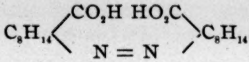
$$\left(C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ NC_2H_4O\end{matrix}\right.\right)_2 \text{ and } \left(C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ NCH_2O\end{matrix}\right.\right)_2.$$

The following reaction would explain these formulas:



$$2C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ NNO\end{matrix}\right. + 2C_2H_4O = \left(C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ NC_2H_4O\end{matrix}\right.\right)_2 + N_2 + 2H_2O.$$

So far as we are aware, no similar decomposition of a nitroso compound has been observed by others. There is some analogy with the formation of acetaldehyde by the action of diazo compounds on ethyl alcohol. It is hoped that further study may lead to a generalization of the reactions and that it may also throw further light on the structure of these compounds.

After filtering off the condensation-product resulting from the action of the methyl alcoholic sodium hydroxide on the nitroso compound, the solution was acidified. This caused the precipitation of a white, solid acid instead of the usual oily mixture. This was washed with ether, in which it is nearly insoluble, and crystallized from alcohol. The amount was about 11 per cent of the weight of the nitroso compound. The substance melts at 327° to 328° (corr.) A nitrogen determination gave 8.32 per cent. Theory requires for the formula $(C_9H_{15}NO_2)_2$, 8.29 per cent. 0.1022 gram required 6.19 cc. of N/10 potassium hydroxide for neutralization. Theory requires for a bibasic acid, having the formula $(C_9H_{15}NO_2)_2$, 6.04 cc. It seems possible that the acid is an azo compound having the structure  $C_8H_{14}\left<\begin{array}{c}CO_2H \quad HO_2C \\ N = N\end{array}\right>C_8H_{14}$. It is hoped to study this compound further.

Johns Hopkins University,
May, 1904.

REVIEWS.

Die Kathodenstrahlen. Von G. C. Schmidt. Braunschweig: Druch von Friedrich Vieweg und Sohn. 1904.

The cathode rays, which were first described by Hittorf more than thirty-five years ago, and brought into prominence chiefly by the brilliant experiments of Crookes, stubbornly refused to give any experimental evidence of their true nature until the study of the ionization of gases by X-rays opened up new lines of attacking the problem. Crookes regarded the rays as flight of molecules driven from the cathode at high velocity and having mean free paths measured in centimeters instead of thousandths of a millimeter. He regarded this condition as a fourth state of matter, to which he gave the name ultra-gaseous. The German physicists however, almost without exception, regarded the rays as a phenomenon of the ether, a view which was strengthened by the failure of Hertz to obtain any trace of a deflection in an electrostatic field, which was to be expected if the rays consisted of charged molecules or atoms, and the experiments of Lenard on the transmission of the rays through aluminium foil.

Though Crookes' original hypothesis has been shown to be untenable, a modification of it, suggested by Schuster, is at the present time almost universally held, the velocities, masses, and charges of the electrons which constitute the rays having been determined with considerable accuracy.

The wide applications which have been made of the electron theory in the domains of physics, chemistry, meteorology, and astronomy, together with the physiological effects of the different types of radiation, make the cathode rays, and the phenomena which accompany them, of interest to workers in almost every branch of science. Professor Schmidt has given us a very concise résumé of the most important work which has been done in clearing up the mystery which has so long hung around the cathode rays, which will prove useful to all who are interested in the development of the modern conception of the "Electron."

The treatment is wholly non-mathematical and is well illustrated with diagrams and cuts. After discussing the various types of apparatus used in the production and study of the cathode rays, the author gives a short review of the various theories which different experimenters have advanced, and the development of the present theory by Schuster, whose theoretical speculation he considers as far eclipsing those of any of his predecessors.

The behavior of the rays in magnetic and electrostatic fields is very fully discussed, together with the methods by which the masses of the moving electrons and their velocities are determined from observations of the deflections of the rays.

In the chapter on the various methods of producing cathode rays, the author omits mention of the fact that Merritt made an independent discovery of the generation of the rays by the illumination of metal surfaces by ultra-violet light, though his paper did not appear until some months after Lenard's. This is doubtless an oversight, for the book is conspicuously free from the tendency shown by some writers to minimize the value of, or ignore completely, work done in other countries. This is especially noticeable in the frequent tribute which he pays to the work of Crookes', which German writers, as a rule, do not seem to have appreciated. While it is true that many of the observations which he made had been previously recorded by Hittorf, he was the first to draw the attention of the world at large to the cathode rays and popularize them by a series of most spectacular experiments, which for the past quarter of a century have been yearly repeated in practically every physical laboratory in the world.

It is to be regretted perhaps that the author has devoted so little space to the emission of the rays by radioactive substances, these cases being the ones upon which interest is chiefly centered at the present time.

The book closes with an allusion to the almost prophetic remark which Crookes made in one of his earlier papers, to the effect that, in his opinion, the greatest scientific problems of the future would find their solution in the realm of "Radiant matter." The establishment of the fact that the disintegration of the radium molecule is accompanied by the emission of types of radiation similar in every respect to those occurring in vacuum tubes seems almost like a verification of this prediction.

R. W. W.

IMMUNE SERA: HÆMOLYSINS, CYTOTOXINS, AND PRECIPITINS. By A. WASSERMANN, M.D., University of Berlin. Authorized translation by CHARLES BOLDUAN, M.D. New York: John Wiley & Sons; London: Chapman & Hall, Limited. pp. 77.

Dr. Bolduan has rendered a real service in translating this little volume of Wassermann, for, of the various summaries of the recent work in this complicated field, this is perhaps the most satisfactory and readable. The title in German is "Hämolysine, Cytotoxine und Präcipitine;" the addition "Immune Sera" in the translation is in a way misleading, for the scope of the work is by no means as broad as implied, and the reader who hopes to find in this little volume a treatise on immunity with a discussion of the various anti-plague, anti-typhoid, anti-diphtheria sera, etc., will be disappointed.

More than two-thirds of the book is taken up with a discussion of the hæmolysins—those substances occurring normally in the serum, and in virtue of which it is capable of dissolving the blood corpuscles of certain other animals. The interest attaching to these bodies comes largely from the fact that an immunity reaction can be obtained with them, *i. e.*, if the blood corpuscles of one animal (A) be injected into another animal (B) the serum of the latter acquires the power of dissolving the corpuscles of A. The results are thus similar to those obtained in many cases with bacteria, and as the experiments can be performed in test-tubes and permit of great accuracy, they offer exceptional opportunities of investigating the laws governing the production of immune sera in general. The work of Ehrlich, which has contributed so largely not only to the collection, but still more to the coordination of facts, is fully discussed in relation to his "side-chain" theory of immunity.

On page 19 it is stated that Ehrlich formulated the "side-chain" theory in order to explain the production of antitoxin and other specific anti-bodies. As a matter of fact the side-chain theory was proposed by Ehrlich nearly twenty years ago, entirely independently of any theory of immunity; through it Ehrlich sought to explain the processes of oxidation in the body. Thus Ehrlich's side-chain theory has a wider biological significance than the reader would be led to suppose from the above statement.

Cytotoxins (other than the hæmolysins) are discussed in the second section. Specific reaction substances can be obtained towards leucocytes, spermatozoa, epithelial, and other cells in the same way as hæmolysins are obtained.

In the third section the author discusses the subject of "precipitins"—those "anti-bodies" obtained by the injection of various kinds of proteids into animals of another species; the serum of the latter acquires the property of forming a precipitate with the form of proteid injected. By this method, in the development of which Wassermann has taken such an important part—it is possible to determine the species of animal from which a given specimen of proteid (*e. g.*, that of human blood) has been obtained, results which seemed unobtainable by any ordinary chemical method. It is perhaps unnecessary to remark that the chemical nature of these "immune bodies" (hæmolysins, cytotoxins, and precipitins) is unknown beyond the fact that they seem to belong to the group of proteids.

The translation has been well done; the advisability of translating "Zwischen-Körper" by "inter-body" may, however, be questioned, the translation "intermediary body" having received the sanction of such authorities as Meltzer, Welch, and Flexner.

To the specialist who desires the very latest developments in this subject, the book cannot be so highly recommended, for the German edition appeared two years ago and contains none of the work published since 1901. Since that time many important papers have appeared, but the fundamental work (*e. g.*, that of Bordet and Ehrlich) is discussed fully and clearly, and what has appeared since has modified this but little. R. H.

LABORATORY EXERCISES IN PHYSICAL CHEMISTRY. By FREDERICK H. GETMAN, PH.D., Fellow by Courtesy in the Johns Hopkins University, Carnegie Research Assistant. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. 241.

This little laboratory guide in physical chemistry will prove to be useful in American and English laboratories, wherever physical chemistry is taught. While several excellent manuals have been published in German there is, up to the present, nothing in English that is adapted to general use.

The subject is treated under thirteen heads: Weighing; Volume and Density; Viscosity and Surface-tension; Solubility; Thermometry; Melting- and Boiling-points; Calorimetry; The Spectroscope; Electrical Units; Resistance; Electromotive Force; Measurement of Current; Measurement of the Dielectric Constant; Chemical Kinetics; and Tables.

Under the last-named head are included quantities which are in constant use in the laboratory.

The book is well-illustrated and well-printed. Omission of letters in headings as on pages 64, 101, and 215 can be easily corrected. The work is heartily recommended to all who are interested in physical-chemical measurements. H. C. J.

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American Chemical Journal.

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